(12) **LEVEL** *III*

AD E 410332

AD

CHEMICAL SYSTEMS LABORATORY CONTRACTOR REPORT

ARCSL-CR-80031

AD A092380

DEVELOPMENT OF A TWO-PIECE MASK AND LENS
AND MOLD FOR SAME

by

Tibor Gabris
Stephan B. King

May 1980

SPRINGBORN LABORATORIES, INC.
Water Street
Enfield, Connecticut 06082

Contract No. DAAA15-77-C-0008

DTIC
ELECTE
DEC 3 1980
S   D

B

US ARMY ARMAMENT RESEARCH AND DEVELOPMENT COMMAND
Chemical Systems Laboratory
Aberdeen Proving Ground, Maryland 21010

394170

8011 07 117

Disclaimer

The views, opinions, and/or findings contained in this report are those of the authors and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.

Disposition

Destroy this report when it is no longer needed. Do not return it to the originator.

REPORT DOCUMENTATION PAGE	READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
ARCSL-CR-80031	AD-A092 380	

4. TITLE (and Subtitle)	5. TYPE OF REPORT & PERIOD COVERED
DEVELOPMENT OF A TWO-PIECE MASK AND LENS AND MOLD FOR SAME	Final Report
	6. PERFORMING ORG. REPORT NUMBER

7. AUTHOR(s)	8. CONTRACT OR GRANT NUMBER(s)
Tibor Gabris Stephen B. King	DAAA15-77-C-0008

9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
Springborn Laboratories, Inc. Water Street Enfield, Connecticut 06082	

11. CONTROLLING OFFICE NAME AND ADDRESS	12. REPORT DATE
Commander/Director, Chemical Systems Laboratory ATTN: DRDAR-CLJ-R Aberdeen Proving Ground, MD 21010	May 1980
	13. NUMBER OF PAGES
	79

14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)	15. SECURITY CLASS. (of this report)
Commander/Director, Chemical Systems Laboratory ATTN: DRDAR-CLW-ED Aberdeen Proving Ground, MD 21010	UNCLASSIFIED
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE NA

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

Contract Project Officer: Gerard H. Denoncourt (DRDAR-CLW-ED, 671-3825)

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Ethylene/propylene elastomer	EVA polymers	Vul-Cup
EPDM	Vynathene polymers	Triallyl cyanurate
EPM, EPR	EY903	Polyurethane polymers
Royalene 100	Elvax 150	Military standard T208
Nordel 1320	Di-Cup	Military standard T209

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Modified contract objective was to screen and modify available elastomers for use as lenses for a mask. Also, a program to bond such a lens to a rubber faceblank was required. Two molds-one faceblank less lens area mold and one lens mold were required. By many tests named in the keywords of this and next pages, a Nordel 1320 vulcanizate; covulcanized Nordel 1320/ Vynathene CY903; Vynathene EY903 vulcanizate; Elvax 150 vulcanizate and LR3-463 polyurethane vulcanizate were selected as final candidates for lens substance. Final candidate appears to be Nordel 1320, 100; Cabosil MS-7.3.0;

DD FORM 1473 EDITION OF 1 NOV 65 IS OBSOLETE

19. KEYWORDS, Contd.

ASTM D637	Adhesives
Optical clarity	Molding cycle
Royalene 521	Acryloid AT-50
Royalene 522	Acryloid AT-56
Nordel 1040	Cymel-325
Vistalon 404	Acryloid A-10
Elvax 40	Acryloid B-50
Vynathene EY903	PPG-5
Chemplex 3000	Tenite 472
Chemplex 3311	Acryloids
Ultimate elongation	Optical uniformity
Compression set	Abrasion test
Long-term storage	Antioxidants
Single-cavity molds	Bonding value
Pellethane 2363-80A	Standard compound 8247-1
DuPont LR3-463	Dirt pickup
Kel F	Brittleness
Viton	Delamination
Kraton 1101	Crosshatch test
A6616	Permeability test
Antioxidant 330	Chemical resistance
Tensile properties	Irganox 1010
SR-350	Irganox MD 1024
Radiation curing	Loctite 420
Flexibility	Transfer molds

20. ABSTRACT, Contd.

Vul-Cup R, 1.5 and Antioxidant 330, 0.5 parts by weight. Loctite 420 was chosen as adhesive for the lens to the faceblank. Photos of the molds and of assembling operations for the two-piece mask are given.

PREFACE

The work performed for this development was required by contract DAAA15-66-C-0008, entitled "Development of a Two-Piece Mask and Lens and Mold for Same". It was carried out from October 1976 to March 1980.

Reproduction of this document in whole or in part is prohibited except with permission of Commander/Director, Chemical Systems Laboratory, ATTN: DRDAR-CLJ-R, Aberdeen Proving Ground, MD 21010. However, Defense Technical Information Center and the National Technical Information Service are authorized to reproduce the document for US Government purposes.

The use of trade names in this report does not constitute an official endorsement or approval of the use of such commercial hardware or software. This report may not be cited for purposes of advertisement.

Acknowledgement

The author wishes to express thanks for the tenacity and ingenuity displayed by Mark Davis and John Labis of the Chem Lab of Springborn Laboratories. Both Mr. Davis and Mr. Labis went beyond the actual scope of the program to resolve problems. Mark contributed much to the better understanding of quality problems we encountered on account of Nordel 1320 batch variations.

Mr. Labis had the tenacity to resolve technical problems associated with assembling a faceblank and a lens material with a 5-second setup time adhesive.

Accession For	
NTIS CRA&I	✔
DTIC TAB	☐
Unannounced	☐
Justification	
By	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A	

CONTENTS

1. INTRODUCTION

The original contract called for the development of an elastomeric, one-piece protective mask. A subsequent modification redirected effort towards the development of a two-piece mask involving separate faceblank and lens components.

An objective of the modified contract was to carry out additional research and development effort to screen and modify commercially available elastomers for use as lenses for the mask.

It was also an objective of this modified program to establish a process for bonding such lens to a rubber faceblank, and to design and fabricate two separate molds – one faceblank less lens area mold and one lens mold.

2. POLYMERS AND CURING SYSTEMS

2.1 Initial Selection. Based on assumed optical clarity, the following polymers were selected as initial candidates for lens material:

Product	Manufacturer
. Ethylene/Propylene Elastomers	
Royalene 521	Uniroyal
Royalene 522	Uniroyal
Royalene 100	Uniroyal
Nordel 1145	Du Pont
Nordel 1320	Du Pont
Nordel 1040	Du Pont
Vistalon 404	Enjay
Vistalon 2504	Enjay
. Ethylene/Vinyl Acetate Copolymers	
Elvax 40	Du Pont
Elvax 150	Du Pont
Resin 3000	Chemplex
Resin 3311	Chemplex
Vynathese EY 903	U.S.I. Chemicals
. Ethylene/Ethyl Acrylate Copolymers	
DPDA 6169	Union Carbide
DPDA 9169	Union Carbide
. Polyurethanes	
Pellethane 2363-80A	Upjohn
Experimental LR3-463	Du Pont
X218-48-1	Upjohn

Product	Manufacturer
. Polysulfide Elastomers	
Thiokol FA	Thiokol
Thiokol ST	Thiokol
. Fluorocarbon Polymers	
Kel-F, low molecular weight	3M Company
Kel-F, high molecular weight	3M Company
Viton	Du Pont
. Thermoelastomers	
Solprene 414	Phillips
Solprene 476	Phillips
Kraton 1101	Shell
Kraton 3202	Shell
Kraton 4122	Shell
Kraton 2104	Shell
. Other Rubber-Related Polymers	
Hypalon 20	Du Pont
Hypalon 45	Du Pont
Hypalon 4085	Du Pont
PNF-200	Firestone
CDB	Exxon

2.2 **Description of the Polymers.** Of the above-listed polymers, only those which showed some promise and/or became final candidates are discussed in detail. The others are only briefly mentioned.

2.2.1 **Ethylene/Propylene Elastomers.** Ethylene/propylene rubber or elastomer is usually called EPDM. The basis for this letter designation is: E - ethylene; P - propylene; D - diene; and M - methylene, which makes up the repeating units (CH_2) in the polymer chain.

Because of the diene monomer (a minor percentage of the total polymer structure, in addition to ethylene and propylene), EPDM elastomers are sulfur-vulcanizable products. However, they also can be cured with organic peroxides.

The less common copolymer of ethylene and propylene (actually the fore-runner of EPDM), containing no diene monomer and no functional unsaturation for sulfur vulcanization, is called EPM. Sometimes this copolymer is called EPR, for ethylene/propylene rubber. This designation is even used to identify the entire category of ethylene/propylene elastomers, including terpolymers and copolymers.

Only one EPM, Royalene 100, was examined under this project, as EPM's did not seem to have the desired characteris tics. The remaining listed ethylene/propylene elastomers were of the EPDM class. Most promising was Nordel 1320.

2.2.2 <u>Nordel Elastomers</u>. The Nordel elastomers are made and sold by the Elastomers Department of DuPont Company. Nordel polymers are based on ethylene, propylene, and 1,4-hexadiene. These monomers are combined in such a manner as to produce an elastomer with a completely saturated backbone and pendant unsaturation for sulfur vulcanization.

The principal difference between the various types of Nordels lies in molecular weight, degree of crystallinity, and diene content - which affect processing characteristics such as hot and cold green strength, and cure rate.

Nordel 1320, an amorphous EPDM polymer of low viscosity (Mooney viscosity of 20), became our most promising candidate of the series of EPDM polymers. In fact, Nordel 1320 became our final candidate for lens vulcanizate, for which reason, this polymer is described in detail under a separate heading.

2.2.3 <u>Royalene</u>. Royalene elastomers are made and sold by Uniroyal. With the exception of Royalene 100, which is an EPM, the types we examined are EPDM rubbers. Our trials with Royalene 100 were not successful.

With regard to Royalene 521 and 522, the only difference between these two polymers is the higher Mooney viscosity of 522, which led us to the decision to carry out experiments with Royalene 521.

2.2.4 <u>Vistalon</u>. Vistalon 404 and 2504 phased out early in our work because of poor optical clarity; therefore, they are not discussed here.

2.3 <u>Ethylene/Vinyl Acetate Copolymers</u>. Ethylene/vinyl acetate copolymers, also referred to as EVA, can be classified by vinyl acetate content. The EVA polymers we examined had the following vinyl acetate contents:

Designation	Supplier	Vinyl Acetate Content (%)
Elvax 40	Du Pont	40
Elvax 150	Du Pont	33
Resin 3000	Chemplex	5
Resin 3311	Chemplex	18
Vynathene EY 903	U.S.I. Chemicals	45

Elvax 40 and Resin 3000, as well as 3311, failed on various screening tests; therefore, they are not discussed here.

2.3.1 <u>Vynathene</u>. Vynathene polymers are manufactured by U.S.I. Chemicals, and are random-structured polymers with vinyl acetate contents ranging from 45-60 percent by weight.

EY 903, a 45 percent vinyl acetate content copolymer, seemed to offer the best all-around properties for our needs. This product was thoroughly evaluated and was retained as a candidate, both on a 100 percent polymer basis and as a blend with EPDM.

Vynathene elastomers are characterized as having moderate to good resistance to oils and solvents. The saturated molecular structure gives Vynathene elastomers very good heat stability and weatherability. This structure also accounts for the virtual immunity of these elastomers to ozone cracking. These polymers, when properly cured, display low compression set characteristics.

Vynathene polymers have a low viscosity which permits rapid compounding at low temperatures. These elastomers are vulcanized with peroxides and can be compounded with conventional rubber processing equipment. The materials can be used for injection molding, compression molding, or transfer molding.

Vynathene elastomers display good resistance to photodegradation at low filler loading. This permits the formulation of weather-resistant compounds in clear formulations. Vynathene polymers have an amorphous structure, which is an advantage for optical clarity. This amorphous structure and the highly stable carbon-to-carbon crosslinks that are obtained with peroxide curing explain the low compression values displayed by these vulcanizates. Actually, compression set values are superior at 100°C to those obtained with tests performed at 70°C.

Vynathene EY 903 is supplied as translucent pellets.

2.3.2 **Elvax.** Elvax resins are manufactured by the Du Pont Company (Plastics Department, Polymer Products Division). The vinyl acetate content of these ethylene/vinyl acetate copolymers ranges from 28 to 40 percent.

From the broad spectrum of Elvax resins, Elvax 40 and Elvax 150 seemed to offer the desired optical clarity. In the final decision, Elvax 150 was retained as a candidate material. Both Elvax 40 and Elvax 150 are high vinyl acetate content resins: Elvax 40 contains 40 percent; Elvax 150 contains 33 percent.

These high vinyl acetate resins, used in hot-melt adhesive and hot-melt coating formulations, provide improved adhesion to nonporous surfaces and have increased solubility in organic solvent. For these reasons they are used in solvent adhesives and in coatings, as well. They are practically never used as an elastomer. However, they are used sometimes as modifiers in elastomer-based hot-melt formulations or in natural rubber or synthetic elastomers to improve resistance to ozone cracking.

The thermal/oxidative stability and compatibility of these high vinyl acetate resins provide a broad formulating latitude. To minimize the possibility of viscosity changes in hot-melt blends during processing (due to eventual oxidation), Elvax 40 and Elvax 150 contain an antioxidant which is an FDA-approved grade of butylated hydrotoluene (BHT).

Elvax 150 is recommended as a component to be used at high concentrations in both paraffin and microwaxes. This compatibility with aliphatic hydrocarbons is probably what explains the good compatibility of this resin with EPDM rubbers, one of our candidate polymers.

Elvax resins are supplied as translucent pellets.

2.4 <u>Peroxide Cure</u>. Organic peroxides were used in our work with ethylenic copolymers like EPDM and EVA, with success. Therefore, it is appropriate to discuss this subject here.

Organic peroxides have been employed as effective crosslinking agents for both elastomers and plastics for decades. Historically, sulfur vulcanization has been, and still is, the preferred method for low-cost compounding of unsaturated rubbers. However, with the ever increasing awareness and use of elastomers as excellent engineering materials, performance rather than cost is becoming the prime consideration.

Peroxide vulcanizates exhibit little or no added color (an important consideration for us); sulfur systems form dark metallic sulfides. Also, sulfur itself tends to depress optical clarity.

Peroxide-induced crosslinks are stable to oxidation. Sulfur crosslinks may oxidize, leading to crosslink rupture. From the standpoint of thermal stability, the peroxide crosslink has a bond energy of 82 Kcal and is as stable as any of the carbon-carbon bonds in the ethylenic polymer backbone. The sulfur crosslink, composed of both carbon-sulfur and sulfur-sulfur bonds, has a lower bond energy and results in a weaker crosslink: the C-S bond energy is equal to 66 Kcal, and that of the S-S bond is equal to 49 Kcal.

Peroxide-cured vulcanizates exhibit higher compression set resistance than do their counterpart sulfur-cured vulcanizates; and peroxide vulcanizates, generally, have better low-temperature flexibility than do sulfur vulcanizates.

Sulfur vulcanization is generally not satisfactory for curing blends of polymers of different unsaturation. Peroxides, being somewhat "blind" to the type of hydrocarbons which they crosslink, are ideal for curing such blends. This was of importance to us because of the work we did on EPDM/ EVA blends.

An important consideration to us is that peroxide stocks can be cured by almost any method - such as compression, transfer, or injection molding. Standard rubber curing equipment can be used without modification for curing peroxide containing stocks.

A class of commercially available peroxides fairly well satisfying the balance of our requirements are diaryl-alkyl peroxides such as dicumyl peroxide (Di-Cup) and α,α '-bis(t-butylperoxy)diisopropylbenzene (Vul-Cup). The chemical formulas of these compounds are:

Di-Cup:

Vul-Cup:

$$H_3C - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - O - O - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - \bigcirc - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - O - O - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - CH_3$$
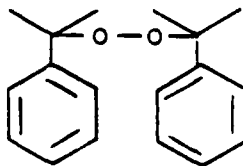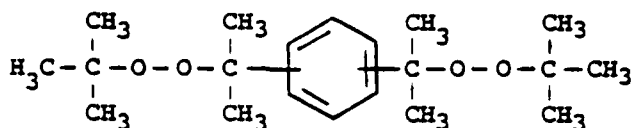
The most commonly used peroxide in the rubber industry is Di-Cup. In our early work with EPDM we used Di-Cup, starting with Di-Cup 40C, an approximately 40 percent active dicumyl peroxide. In Di-Cup 40C the dicumyl peroxide is supported on precipitated calcium carbonate. Because of this, it is easier to disperse than is straight dicumyl peroxide (Di-Cup R).

Di-Cup rapidly decomposes in the compound on heating and effects a good, tight cure but develops a decidedly objectionable odor. This is caused by the normal by-product of dicumyl peroxide decomposition, acetophenone. The odor might be considered less unpleasant than different from the odor normally associated with other methods of vulcanization.

We found that the calcium carbonate contained in Di-Cup 40C depressed the optical clarity of the EPDM; for this reason we switched to Di-Cup R (98 to 100 percent active dicumyl peroxide).

In order to improve on the odor situation, we heat-treated the finished vulcanizates, which definitely helped; still some residual odor was noticeable after the heat treatment. We therefore looked for an alternative, odor-free peroxide curing system, and thus switched to Vul-Cup R.

Vul-Cup R is 96 to 100 percent active peroxide. At room temperature Vul-Cup R is a tan to yellow-white colored semicrystalline solid. It varies in isomer ratio from 1.5:1.0 to 2.0:1.0 in meta:para content. Melting point range of the commercial product, Vul-Cup R, is dependent on isomer ratio, assay, and type of nonperoxidic components. The typical metling point normally falls within the range of 45-55°C.

Vul-Cup may be substituted for Di-Cup on an equivalent peroxide weight basis to give equivalent state of cure. Vul-Cup decomposes thermally when heated to form peroxy radicals that, in turn, abstract hydrogen from the polymer backbone, forming polymer radicals. A combination of two of these polymer radicals results in a crosslink.

The efficiency of a peroxide is determined by the number of crosslinks obtained per mole of peroxide used. Several factors affect the efficiency of peroxides in rubber; these include: type of peroxide; rate of thermal decomposition ("half life"); type of polymer or the medium in which the peroxide decomposes, and therefore other additives present in the stock; cure time; and cure temperature.

Full development of the tensile strength of the vulcanizate, hardness, and good compression-set resistance are not achieved when the use level of the peroxide is below the optimum. Higher use levels result in some loss of properties. Excessively high levels generally leave part of the peroxide unreacted. This can have an adverse effect on compression set and on the aging of the vulcanizate. Therefore, in each specific application the optimum

level of peroxide should be determined for best balance of properties, just as was determined with Vul-Cup R for our specific needs.

Co-curing agents such as methacrylate monomers, triallyl cyanurate, etc., can be used as additives in peroxide formulations to modify and/or improve properties of the vulcanizates. We explored this and retained some of these agents in our final formulations (as will be seen later in this report).

2.5   Ethylene/Ethyl Acrylate Copolymers. Two copolymers from Union Carbide which had different melt indexes were examined as potential candidates: DPDA 6169 and DPDA 9169. Both polymers contain 18 percent ethyl acrylate.

These copolymers were tried in both the uncured and the peroxide-cured forms, as well as in blends with EPDM. The optical properties of these compositions were disappointing; therefore, these copolymers are not discussed in detail.

2.6   Polyurethanes. Most commercially available polyurethane elastomers are based on low molecular weight polyester or polyether polymers that are terminated with hydroxyl groups. The other starting materials or intermediates consist of di- or polyfunctional isocyanates and, with most systems, low molecular weight polyfunctional alcohols or amines.

The liquid starting polymer is generally in the range of 500 to 3,000 molecular weight. Variations in the characteristics of this starting low molecular weight polymer and the concentration, type, and arrangement of the isocyanate and other small molecules used for chain extension provide a board range of different polyurethane elastomers.

Two polyurethane polymers were examined under this program: LR3-463 and Pellethane 2363-80A.

2.6.1   LR3-463. This is an experimental, heat-curable thermoplastic urethane polymer developed by Du Pont and examined earlier by the Chemical Systems Laboratory (CSL). We had requested and received from Du Pont 6 pounds of improved LR3-463. It is to be recalled that this is the polyurethane which had already passed a number of tests (see CSL files).

The material reached us in a cast sheet form. According to Du Pont (L. Ahramjian, research chemist), the vulcanizate properties on this batch of polymer were as follows:

Modulus at 100 percent elongation	200 psi
Tensile strength at break	3000 psi
Elongation at break	540 percent
Permanent set	5 percent
Die B tear strength	200 pli
Compression set, 22 hr/70°C	39 percent

2.6.2 <u>X218-48-1</u>. This new, castable-type polyurethane from Upjohn seemed to be promising. The hardness of this polymer was expected to be close to 55 Shore A. Our intention was to test this polymer in cast form, then (provided it showed further promise) modify it for transfer or injection molding.

Upjohn was asked to supply some X218-48-1 in 10-mil sheet form for our work. After the samples were received, however, their optical clarity changed in storage to high haze. Also, it was noticed that marking inks penetrated into the polymer phase and caused severe staining.

In view of the above, it was decided to do no work with this polymer.

2.6.3 <u>Pellethane 2363-80A</u>. This is an injection-moldable grade polyurethane manufactured by Upjohn, a difficult-to-mold polymer of high hardness (Shore A 80). While the hardness of this polymer was definitely too high for our purpose, its other properties warranged its evaluation. It was also hoped that its hardness could be reduced by proper compounding.

2.7 <u>Fluorocarbon Polymers</u>. These polymers are not i-purpose materials; indeed, they perform quite poorly under certain conditions and in certain environments where cheaper rubbers or plastics are necessarily selected because of their optimum performance. Presently, these polymers are the most expensive elastomers and plastics - ranging from $10 to even $60 per pound at specific gravities as high as 1.85.

2.7.1 <u>Kel-F</u>. Kel-F polymers are manufactured by 3M Company. Both Kel-F 6060 and Kel-F 6061 are plastics. They could be described as crystallizable but never completely crystalline polymers. According to the supplier, Kel-F 6060 and 6061 are identical products except for physical form: Kel-F 6060 comes in pellets; Kel-F 6061 is a powder.

We tried to take advantage of some of the attractive properties of Kel-F by special molding techniques and by compounding. The attempts were not successful. Therefore, no further attention is devoted to these polymers in this chapter.

2.7.2 <u>Viton</u>. This fluorocarbon rubber, made by Du Pont, is a copolymer of vinylidene fluoride and hexafluoropropylene. Viton polymers range widely in molecular weight. For example, Viton A and AHV run from 100,000 to 200,000. Viton LM, a waxlike material, has a molecular weight of less than 5,000.

We examined Viton because of the promising results obtained by radiation curing as reported by Lipko and Sperling. Our attempts to cure Viton by conventional methods did not yield attractive compounds for this project; it evolves that radiation curing does not seem to be a practical or large-scale manufacturing method for our use, and this is true for Viton.

2.8 <u>Thermoelastomers</u>. Thermoplastic elastomers (thermoelastomers) are polymers in which the end-use properties of vulcanized elastomers are combined with the processing advantages of thermoplastics. These polymers are thermoplastic but rubbery and yield a product with the properties of vulcanized rubber, without any kind of cure or aftertreatment.

In general, these thermoplastic elastomers are block copolymers. The only commercially available thermoelastomers, at present, are styrene-isoprene-styrene and styrene-butadiene-styrene copolymers.

Theremoelastomers exhibit the tensile properties typical of rubber vulcanizates. Another characteristic of the thermoplastic elastomers is resilience. The compression set of thermoelastomers is high by vulcanized rubber standards, and increases rapidly with temperature.

Although the thermoelastomers are supplied in the market as ready-to-use materials, they can be compounded to modify the properties of the thermoelastomer. In general, reinforcement of the thermoelastomers is unnecessary, since this is provided by the domain structure of the polymer; thus, reinforcing fillers like silica are not required in thermoelastomers. Such reinforcing fillers may be used, however, if some other property is contributed.

As will be noted, several thermoelastomers were tried; however, none of them tended to yield the required optical features or agent resistance. They were tried also as modifying agents for other polymers, and were also examined in peroxide-cure form. None of these experiments gave satisfactory results.

2.9   Other Rubber-Related Polymers. Tried were: Hypalon, which chemically is chlorosulfonated polyethylene; PNF-200, a new elastomer, chemically a phosphonitrilic fluoro compound which is presently marketed at a price of $100/lb; and the CDB (conjugated diene butyl) technology of Exxon. These polymers failed on the optical clarity requirements. Consequently, no attention is devoted to these polymers in this chapter. The results of these experiments are discussed elsewhere in this report.

3.   PREPARATION FOR TESTING

The polymers were either simply sheeted out or compounded and then sheeted out on a differential-speed roll mill having a front roll speed of 21 rpm and a back roll speed of 27 rpm. The mill friction ratio was 1.28.

At a later stage of the program, and more specifically when larger quantities of the final candidates were being produced for testing, Banbury equipment having a maximum working capacity of 1100 cc was used for compounding the EVA and EPDM batches.

All compounding and sheeting was done on a cold mill and Banbury batches were made in cooled equipment. It has been confirmed that with proper cooling of the Banbury using a stepwise cycle, EPDM and EVA compounds can be made without difficulty.

Samples of appropriate thickness (75 mils for most ASTM tests, and 100 mils for others) were compression molded using standard rubber molds and hydraulic presses equipped with electrically heated platens. No mold release agent was used on specimens prepared for optical tests since mold release agents have an adverse effect on optical clarity (in particular, haze). The compression molding, unless otherwise indicated, was done with the aid of nickel plates.

4.   TESTING METHODS

Many of the routine tests (light transmission, haze, compression set, tensile strength, etc.) were executed in accordance with ASTM test methods, which are not described here but are briefly mentioned under the paragraphs dealing with the screening of the candidate materials.

Some of the less common tests we used for the purpose of screening and acceptance are described herein.

4.1   Chemical Test. The lens materials (candidates) were subjected to gasoline, diesel fuel, ethyl alcohol, insect repellant, etc., and were examined for blistering, crazing, or other appreciable change. In these tests, five (5) drops of the chemical were placed in the center of the test specimen. After 5 minutes the chemical was removed by blotting and the surface was inspected for degradation.

4.2   Agent Resistance/Permeability. Agent permeability was determined in accordance with a modified version of MIL Standard Methods T208 and T209 (GB Resistance of Impermeable Materials and Mustard Resistance of Impermeable Materials, respectively, Static Diffusion Method). As an exception, in accordance with contract specification (2)(e) "Permeability", methyl ethyl ketone (MEK) and cyclohexylamine were used as indicators of permeability of the candidate materials.

According to the specifications, elastomers which pass more than 4 γ/ cm^2 MEK or 1.25 γ/cm^2 cyclohexylamine in a 360-minute period should be eliminated from the study.

In our tests, the material (100 mil thick sheet) was placed between two reaction vessel covers (see Figure 1) and approximately 2 milligrams of either MEK or cyclohexylamine introduced into the upper chamber. This was left to penetrate for 6 hours. Meanwhile, a charcoal tube connected to a personal sampling pump was pulling air from the outside through the bottom portion of the reaction vessel (cover). Any solvent passing through the material being tested is collected and adsorbed on the charcoal tube. For the MEK analysis, the charcoal tube was desorbed with 1 milliliter of CS$_2$. A calibration curve was made using known amounts of MEK in CS$_2$. Specifically, in one set of tests 0.26 mg/ml, 0.53 mg/ml, and 1.6 mg/ml were used as standards.

The maximum value to pass the test was 0.53 mg/ml, calculated from the requirement that the maximum limit was to be 4 γ/cm^2.

> Detector: FID
> Column: 10% FFAP (20' x 1.8") on 80/100 mesh acid washed
>   DCMS Chromosorb W
> Hydrogen flow: Approximately 30 ml/min.
> Air flow: Approximately 300 ml/min.
> Nitrogen flow: Approximately 30 ml/min.
> Injection temperature: 200°C
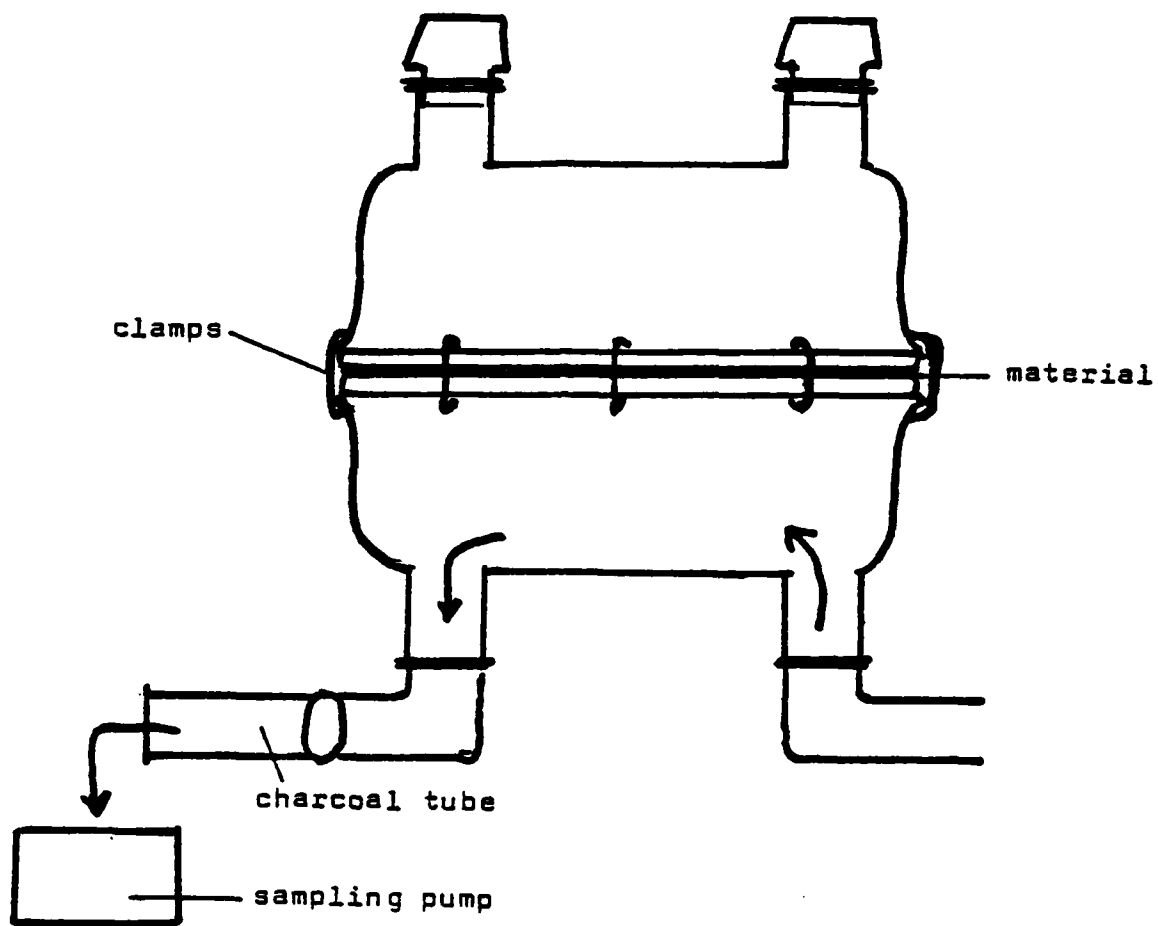> Detector temperature: 200°C
> Column temperature: 80°C

16

Figure 1. Apparatus for Testing Permeability

For the cyclohexylamine analysis, silica gel tubes were used. The procedure was the same as for the MEK analysis except that the cyclohexylamine was collected on these silica gel tubes, packed with three sections of 45/60 mesh silica gel, and adsorbed using 95 percent ethanol.

Again, a calibration code was made using known amounts of cyclohexylamine in ethanol - specifically, 11 ppm and 22 ppm. A value of 16 ppm or less passed the test. These values were later reconverted to γ/cm^2 to be in agreement with the MEK data. The 16 ppm figure was obtained from the requirement that the maximum value per sample was to be 1.25 γ/cm^2. This means that, for example, with an area of 132.6 cm^2 the maximum allowable value is 167.75 γ.

The GC conditions for these costs were as follows:

Detector: FID
Column: 6' x 1/8" SS, Crom 103, 80/100 mesh
Column temperature: 190°C
Injector temperature: 235°C
Detector temperature: 250°C
Hydrogen flow: 28 ml/min.
Air flow: 300 ml/min.

4.3   Optical Uniformity. Optical uniformity of the candidate lens materials was tested in accordance with ASTM D637 (Surface Irregularities of Flat Transparent Plastic Sheets). The method makes use of the prismatic or optical-wedge deflection of a beam of light as it passes through a distortion spot or wave in the body of or on the surface of the material being inspected.

The candidates were examined for three features: (1) displacement factor, (2) frequency of image movement, and (3) pattern distance.

The apparatus we used for these tests was an ordinary lantern slide projector, with which we projected the image of a cross on a screen. This cross served as our reference point for the tests.

Displacement factor was determined as the maximum movement (inches) of the image of the cross, divided by the distance (feet) from the projector to the screen, multiplied by 1000.

Frequency of image movement is described as: "irregular", "wavy", "frequent", or "single shift".

5.   PRELIMINARY SCREEI IG TESTS AND RESULTS

The two properties most critical to the development of an elastomeric protective mask (original contract) and/or lens material (contract modification) are transparency and agent resistance. To systematically eliminate candidates and to narrow down to those polymers which showed promise, we ran tests on optical clarity, chemical resistance, and permeability.

18

It is to be noted that this contract actually consisted of two parts: the original contract, and a modification. The criteria (screening tests) changed somewhat as the modification of the contract went into effect. An attempt will be made in this chapter to present these tests in a logical, combined form.

5.1 <u>Optical Clarity - Visual Examination</u>. Specimens were first examined visually for optical clarity. Candidates which failed on this test were eliminated, while candidates which displayed good optical clarity were retained for further testing.

5.1.1 <u>Ethylene/Propylene Elastomers</u>. Uncured samples of both Nordel 1145 and Vistalon 2404 failed on this test. Royalene 100 failed both in uncured and peroxide-cured (silica-filled) form. We retained for further testing the following polymers:

Royalene 521 (and 522)
Nordel 1320 and 1040
Vistalon 404

5.1.2 <u>Ethylene/Vinyl Acetate Copolymers</u>. Both uncured Elvax 40 and uncured Elvax 150 displayed excellent optical clarity. Vynathene EY 903 as well as Chemplex 3000 and 3311 displayed good optical clarity. Thus, all five EVA candidates were retained for further tests.

5.1.3 <u>Ethylene/Ethyl Acrylate Copolymers</u>. No attractive optical clarity could be obtained from DPDA 6169 and DPDA 9169, either in the uncured or the peroxide-cured form. These polymers were also evaluated as eventual modifying agents to upgrade the physical properties of peroxide-cured EPDM vulcanizates. The molded plaques were very hazy. Consequently, no further work was done with these co-polymers.

5.1.4 <u>Polyurethanes</u>. Both Pellethane 2363-80A and Du Pont LR3-463 displayed good optical clarity. They were therefore retained for further work. X218-48-1 turned hazy after some storage and was therefore discarded as a potential candidate.

5.1.5 <u>Polysulfide Elastomers</u>. Both Thiokol FA and ST displayed very poor optical clarity; therefore these polymers were not considered for additional testing.

5.1.6 <u>Fluorocarbon Polymers</u>. Both Kel-F and Viton displayed fair optical clarity, to justify further testing.

5.1.7 <u>Thermoelastomers</u>. Kraton 4122, 3202, and 2104 badly failed on optical clarity. Since the optical clarity of Kraton 1101 could be improved by high-temperature milling, this polymer was retained for further work.

5.1.8 <u>Other Rubber-Related Polymers</u>. Three polymers, Hypalon 20, 45, and 4085, were tried in both the uncured and the cured form. None of these combinations passed the optical clarity tests. The same was true for Firestone's PNF-200, and CDB compounds made in accordance with the Exxon technology.

5.2   Optical Clarity - Measured on Uncured Polymers. As can be seen from
the previous section, the following polymers were retained for further tests:

        Nordel 1040*
        Nordel 1320
        Royalene 521*
        Elvax 40*
        Elvax 150
        Vynathene EY 903
        Chemplex 3000
        Chemplex 3311
        Pellethane 2363-80A
        Du Pont LR3-463 (not examined in the uncured form)
        Kel-F 6060
        Kel-F 6061
        Kraton 1101*

        *Under the old (original) contract, we used MEK overnight immersion
         test as a screening method. These polymers did not pass this test
         so they were not examined for optical clarity in the uncured form.
         They were, however, tested in the cured form.

        Light transmission and haze were determined on these polymers in the
uncured stage. The results are shown in table 1.

Table 1. Optical Clarity of Uncured Polymers

Polymer	Light Transmission (%)	Haze (%)
Nordel 1320	49	70
Elvax 150	81	17
Chemplex 3000	37	76
Chemplex 3311	81	13
Vynathene EY 903	83	16
Pellethane 2363-80A	81	8
Kel-F 6060	65	13
Kel-F 6061	62	17

5.3   Optical Clarity - Measured on Compounded/Cured Polymers

5.3.1   Vynathene EY 903. Vynathene EY 903 was evaluated both by curing with Vul-
Cup R alone and by curing with a combination of Vul-Cup R and triallyl cyanurate
(TAC) as an activator. Optical clarity values on these vulcanizates are as shown
in table 2.

Table 2. Optical Clarity of Vynathene EY 903 Vulcanizates

Composition of Compound*		Light Transmission (%)	Haze (%)
Vul-Cup R	TAC		
1.0	-	75	11
1.0	1.0	77	14

Cure: 15 minutes at 350°F

* Parts per 100 parts Vynathene EY 903

The Vul-Cup R/TAC vulcanized Vynathene compound did not meet optical clarity requirements. This compound, however, had a number of qualities (see other sections of this report) which warranted further work. Also, optical clarity of the vulcanizate could be improved somewhat by milling. This compound therefore became one of our early candidates (A6996).

Although, in general, it was observed that the optical clarity of Vynathene EY 903 can be improved by milling, it was also observed that Vul-Cup cure has an adverse effect on the optical clarity of the Vynathene; however, such cure is needed to obtain high physical properties.

5.3.2   Elvax 150. The encouraging results obtained on uncured Elvax 150 prompted us to evaluate a peroxide-cured Elvax 150. Our best results were obtained on the following formulation:

	Parts by Weight
Elvax 150	150.0
SR-350	2.0
Vul-Cup R	1.5

Cure: 15 minutes at 350°F

Because of its window-glass appearance and good physical properties, this vulcanizate became one of our candidates; it is referred to as A7717.

Elvax 150 is a typical hot-melt adhesive polymer which caused considerable molding problems. Seventeen different approaches were tried for properly molding this compound (the results of these experiments are tabulated in Table 1 of our repc. dated January 25, 1978). The optical clarity of this vulcanizate was as follows:

Light transmission, %   -   92

Haze, %   -   3

21

5.3.3 Du Pont LR3-463. This experimental polyurethane was molded in a curing cycle of 10 minutes at 301°F (150°C). The material tended to stick to the nickel plates; therefore, attempts were made to cure between Mylar foils and Teflon-coated plates, respectively.

Most of the Mylar was easy to remove from the cured plaques; however, there was a tendency for the Mylar to stick to the surface in spots which displayed a high haze while the remainder of the surface of the plaque had very good optical clarity. Our attempt to cure between Teflon-coated plates failed, despite the newly coated plates: the resulting cured specimens displayed high haze and had a lower light transmission that resulted when the plaques were cured between Mylar. The results of these experiments are shown in table 3.

Table 3. Optical Clarity of Cured LR3-436

Conditions	Light Transmission (%)	Haze (%)
Cured between Mylar sheets	88.5	5.9
Cured between Teflon-coated sheets	79.3	44.6

It is interesting to note that LR3-436, in uncured form, also displays high haze. This haze, however, disappears as the urethane is cured.

5.3.4 Kel-F 6060 and 6061. Both Kel-F polymers had a high hardness for our purpose. Attempts were made to plasticize Kel-f with Halocarbon Oil, which product left no plasticizing effect. It is conceivable that a significant portion of the Halocarbon Oil flashed off at the molding temperature. We therefore evaluated a higher molecular weight version of this product: Halocarbon Wax. No plasticizing effect could be observed. On the other hand, the resulting plaques displayed very high haze and a tan color.

Our attempts to plasticize Kel-F 6060 or 6061 with Kel-F Elastomer 800 failed, also. The resulting compound was not homogeneous and its optical clarity was poor.

5.3.5 Plaques were prepared by mill-mixing Viton (sent to us by CSL) with 3 parts of a trimethyl propane product suggested by Sperling and Lipko (see their draft submitted to CSL). Moldings were made at 250°F and 325°F, respectively. It was foreseen that radiation curing would be applicable for such vulcanizates.

Our attempts failed, as the molded Viton compound displayed a yellow/light brown color. We found that Sperling and Lipko's work was restricted to the use of a small internal mixer blanketed with nitrogen, following which the molded compound was transferred between Mylar sheets for radiation curing. We felt that this kind of operation is not practical for large-scale production, and we therefore did not explore this route any further.

5.3.6 Polymer Blends. Thermoelastomers - Thermoelastomers have quite good physical properties. These polymers, however, failed in our previous work both on light transmission and haze.

As hot milling improved the optical clarity of Kraton 1101, we reexamined this elastomer, both as an additive to upgrade EPDM elastomers (physical properties) and as a peroxide-cured compound. Kraton 1101 cured with Vul-Cup R passed some of the chemical tests (as will be seen later in this report), but the vulcanizate badly failed on optical clarity: 49 percent light transmission and 30 percent haze. Blends with Nordel 1320 yielded some rather milky vulcanizates, indicating a low compatibility of Kraton with EPDM.

Also, the Solprene yielded some very milky vulcanizates - either as a peroxide-cured polymer or when covulcanized with Nordel 1320. This could not be improved on by incorporating silica nor by using a vinyl silane (A-172) coupling agent.

EPDM/EVA Blends - Results of some preliminary tests indicated that some of the EVA copolymers combined with EPDM could become candidates. On this basis, EVA/EPDM cuts were compounded with silica and cured with Vul-Cup R. Ratios of 30/70 and 50/50 EVA/EPDM were tried. No effort was made to evaluate higher ratios since our experience indicates that higher ratios impair optical clarity and cause high hardness of the vulcanizate.

The optical clarity of these blends is shown in table 4.

Table 4. Optical Clarity of EVA/EPDM Blends

Composition*	Light Transmission (%)	Haze (%)
Vynathene 903/Nordel 1320, 50/50	78	22
Vynathene 903/Nordel 1320, 30/70	82	9
Elvax 150/Nordel 1320, 50/50	74	46
Elvax 150/Royalene 521, 50/50	79	30
Elvax 150/Royalene 521, 30/70	80	16

* Cured with Vul-Cup R at 350°F for 15 minutes;
  EPDM fraction contains 3 parts silica/100 parts EPDM.

As can be seen, the 30/70 Vynathene EY 903/Nordel 1320 proved to be a combination that displayed an attractive optical clarity. This vulcanizate became one of our early candidates under reference number A6992.

At a later stage of this program, Nordel 1320 was reexamined in combination with Vynathene 903 to improve physical properties of the Nordel. Since low temperature flexibility of the blends suffer at the 30 parts Vynathene 903 level, tensile/elongation properties of blends made with smaller amounts of Vynathene 903 (25 parts Vynathene 903/75 parts Nordel 1320, etc.) were examined.

By this time, we included minute quantities of an antioxidant since we wished to improve aging properties of the Nordel fraction. (As will be seen later, some aging problems have been experienced with the Nordel 1320 vulcanizate for which reason Antioxidant 330 was systematically included in the Nordel formulations. More on this later in this report).

Results of these tests are shown in the next chart (figure 2). As will be seen, the tensile strength of the Nordel 1320/Vynathene 903 vulcanizate does not increase significantly before 25 parts of Vynathene are introduced. For these reasons, further work with the Nordel 1320/Vynathene 903 blends was discontinued.

Chemplex 3311 displayed fair optical clarity in uncured form. It was hoped that this polymer could upgrade physical properties of our Nordel candidate, A6150C. In view of the encouraging results obtained on 70/30 Nordel 1320/EVA blends, the same ratio was tried with Chemplex 3311.

No homogeneous compounds could be obtained on the mill: the mill batch showed signs of phase separation of Nordel 1320 and Chemplex 3311. Consequently, the optical clarity of the vulcanizate was poor: 70 percent light transmission and 33 percent haze.

5.3.7 **Additives.** Considerable effort was devoted to studying vinyl silane as a possible agent to improve optical clarity of silica-filled EVA/EPDM vulcanizates. For better understanding, we also examined this in a well established EPDM formula.

No significant difference could be observed in our formulation 6150C, a well established Nordel 1320 compound containing silica and cured with Vul-Cup R. In fact, light transmission and haze suffered somewhat, probably because of the blooming out of the vinyl silane. A brief study (varying the amount of A-172) confirmed the very limited compatibility of this agent with the Nordel. The situation was similar with the various Elvax/Nordel and Vinathene/Nordel vulcanizates. Some of the vulcanizates, which had fair optical clarity after molding, developed a slight haze after a few days' storage.

An attempt was made to replace our currently used silica (Cabosil) with another grade to improve optical clarity of EPDM vulcanizates. PPG's HiSil 215 was used in place of Cabosil in our formulation 6150C. The vulcanizate yielded a light transmission and haze both inferior to formulations made with Cabosil. Therefore, no further work was done with HiSil 215.

There were indications (U. S. Rubber study) that certain imidazolines can act as dispersing agents for silica in EPDM rubber. A better dispersion of the Cabosil could have improved optical clarity. Also, it could have resulted in some improvement in tensile.

The most promising additive to disperse the silica with good efficiency, and to do so in an EPDM compound, is an imidazoline prepared by the condensation of oleic acid and aminoethylethanolamine. This compound is commercially available from Emery Industries under the designation Imidazoline 9885.
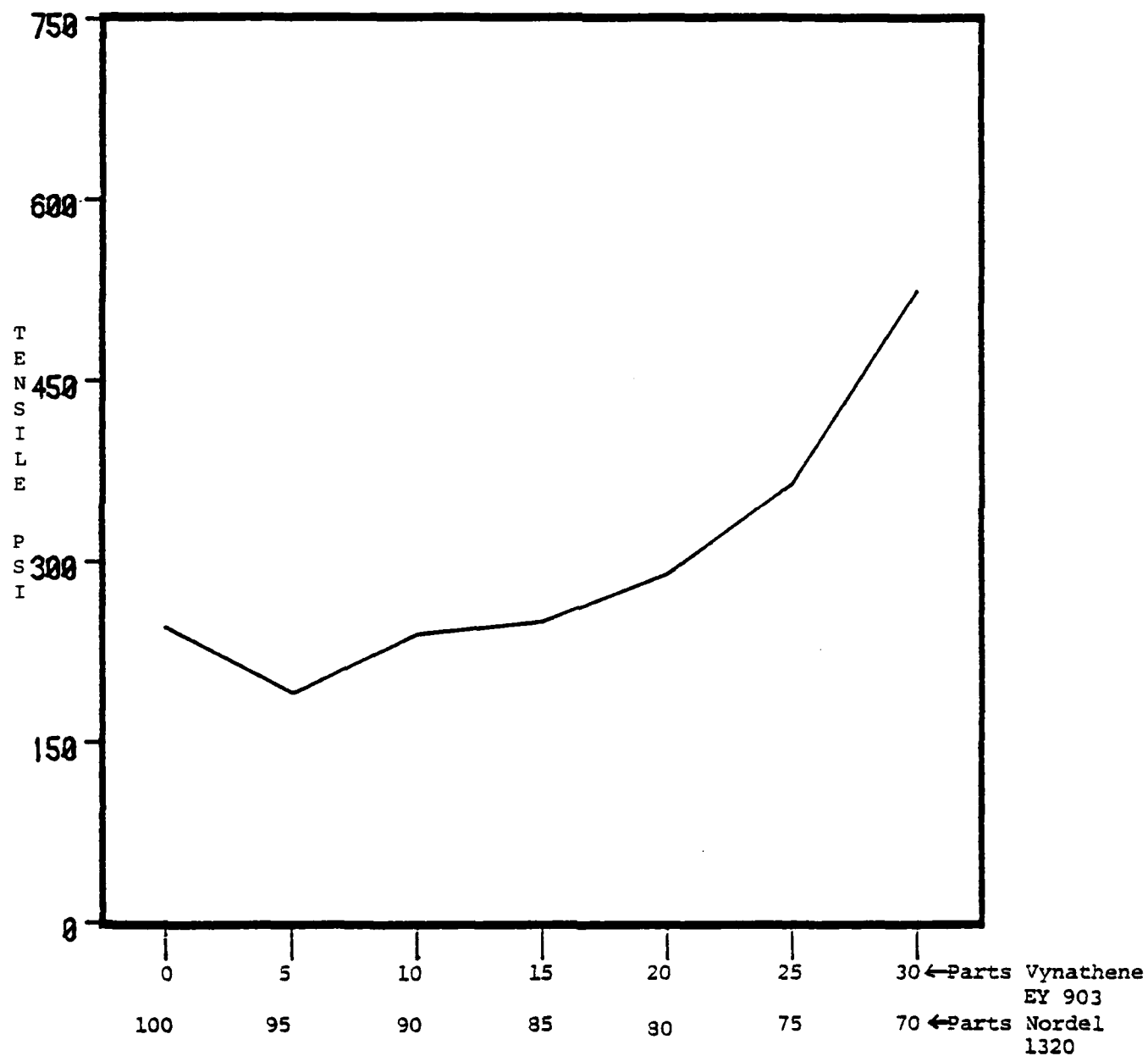
VYNATHENE EY 903/NORDEL 1320 BLENDS

Figure 2. Tensile Properties:
Vynathene/Nordel Blends

An attempt was made to mill this imidazoline into the regular 6150C compound. Considering the small amount of silica involved (3 parts), it was difficult to introduce the corresponding amount of imidazoline. It was equally difficult to distribute this minute amount properly. No improvements of physical properties could be observed between the standard and imidazoline-modified 6150C vulcanizates.

In another attempt, the imidazoline was first masterbatched in Nordel (95% Nordel 1320 and 5% imidazoline). A third attempt was made by dissolving the imidazoline in hexane. Then, the silica was treated with this imidazoline solution before milling into the 6150C compound.

The latter method must have yielded a very uniform distribution of the imidazoline on the silica. Only a slight improvement in the tensile properties could be confirmed, however.

A formulation was evaluated in which the silica (Cabosil MS-7) was increased from the usual 3 parts to 15 parts. This was done both with and without the help of a hexane solution of imidazoline. Results were not encouraging.

5.3.8 **Nordel 1320.** This elastomer became one of our final polymer candidates - both in compounds, in which Nordel 1320 was the sole polymer, and in polymer blends. Acceptable vulcanizates were made with the help of minute amounts of silica as a reinforcing filler, and organic peroxides as the curing agent.

As described earlier, Di-Cup was used in our initial work, as the peroxide curing agent. Because of odor problems, we switched later to Vul-Cup R, staying with this peroxide for the remainder of our work.

Our basic formula for this intermediate Nordel 1320 candidate, referred to as 6150C, had the following formulation:

	Parts by Weight
Nordel 1320	100.0
Cabosil MS-7	3.0
Vul-Cup R	1.5

Cure: 15 minutes at 350°F

Several approaches were tried for the purpose of obtaining the maximum all-around properties (optical clarity/tensile/compression set, etc.) from a Nordel 1320 vulcanizate. Included were the evaluation of acetone-extracted Nordel 1320 (to eliminate processing aids and thus increase the optical clarity), the evaluation of polyfunctional monomers such as SR-350, the elimination of mold-release agents, step-cure, etc. Results of these tests are presented in table 5.

Table 5. Optical Clarity of Nordel 1320 Vulcanizates

Composition of Nordel 1320 Compound[*]						Curing Cycle (°F/min)	Light Transmission (%)	Haze (%)
Acetone Extracted	Di-Cup	Vul-Cup	Sil-ica	SR 350	Mold Release Agent			
No	2.5	-	-	-	Yes	350/15	72.5	12.8
No	2.5	-	-	-	Yes	350/5+ 370/10	85/3	5.3
No	2.5	-	3.0	-	Yes	350/15	82.4	9.3
Yes	2.5	-	-	-	Yes	350/15	82.8	19.9
No	-	1.5	3.0	-	No	350/15	90.0	2.2
No	-	1.5	3.0	2.0	None	350/15	86.6	3.9
No	2.5	-	3.0	2.0	No	350/15	70.2	11.5
Yes	2.5	-	3.0	2.0	Yes	350/5+ 370/10	85.3	7.0
No	-	1.5	3.0	-	Yes	350/15	88.0	5.2
No	-	1.5	3.0	2.0	None	350/15	86.0	3.9
No	-	1.5	6.0	4.0	None	350/15	79.2	12.3
No	-	1.5	6.0	-	None	350/15	-	-
No	-	1.5	3.0	4.0	None	350/15	82.5	6.5
No	-	1.5	-	2.0	None	350/15	71.4	42.3
No	-	1.5	3.0	4.0	None	300/5+ 370/10	77.4	6.4
No	-	1.5	6.0	4.0	None	300/5+ 370/10	74.6	9.6
Yes	-	1.5	6.0	-	None	300/5+ 370/10	-	-
Yes	-	1.5	6.0	4.0	None	300/5+ 370/10	76.8	7.7

* Parts per 100 parts of Nordel 1320

The aging problems (desert-aged) we experienced with 6150C vulcanizates made us initiate a program to test certain antioxidants. Details of this study are discussed elsewhere in this report.

6.   SURFACE TREATMENT

To cut dust pickup of the Nordel lens material (6150C and later antioxidant modified vulcanizate 8247-1), several approaches have been examined.

6.1   Chlorination. A chlorine bath was made by saturating water with chlorine gas. The lens material vulcanizates were immersed in the bath over the weekend.

The specimens turned opaque. An oven treatment of $350^\circ F$ for 20 minutes produced changes; the vulcanizate turned dark brown but transparent. Less severe treatments (chlorine bath for 1, 2, and 3 hours) did cut the dust pickup but not significantly.

6.2   Postcuring. Samples of the cured lens material were postcured for 10, 20 and 30 minutes at $300^\circ F$ and $350^\circ F$. No significant improvement to "tightness" of surface could be noticed. Color formation was evident, especially at $350^\circ F$.

6.3   Peroxide/Antioxidant Treatment. Vul-Cup R solutions (2%) were soaked into the vulcanizate and postcured at various temperatures. Also Vul-Cup R/ Antioxidant 330 solutions were prepared and soaked into the vulcanizate and postcured. No significant improvement could be noticed. Again, yellowing was noted with exposure to higher temperatures for longer periods of time.

6.4   Radiation Curing. In an attempt to upgrade surface quality and physical properties, several materials were subjected to high energy electron beam curing. These were:

Nordel 1320 compounded with 3 parts Cabosil MS-7
(molded between FEP sheet; not vulcanized);

Standard, vulcanized 6150C;

Vulcanized 8247-1 (6150C with 0.5 parts Antioxidant 330).

These materials were irradiated with 2.5 Mrads (one pass), 5.0 Mrads (two passes), and 7.5 Mrads (three passes).

The Nordel 1320/Cabosil MS-7 composition, when irradiated with 2.5, 5.0 or 7.5 Mrads, tends to produce bubbles. No physical properties could be measured on these irradiated samples due to the intensive presence of bubbles.

Both, the standard 6150C vulcanizate and 8247-1, the one made with 0.5 parts Antioxidant 330, irradiated with 2.5 Mrads showed some improvement in surface quality (reduced dust pickup). Further irradiation (5.0 or 7.5 Mrads respectively) does not appear to significantly improve surface quality.

The effect of irradiation on tensile properties is minimal. Thus, the state of cure does not appear to be further advanced by irradiation. It should be pointed out, however, that the state of cure of the peroxide-cured vulcanizates - as measured by gel-content determination, was found to be high already.

One interesting observation is that the physical properties of the vulcanizates containing Antioxidant 330 are essentially the same as those of the vulcanizate without Antioxidant 330 (6150C). It has been determined previously that 0.5 parts Antioxidant 330 in standard 6150C compound gave a vulcanizate with 240 psi tensile.

While these slight improvements in tensile properties could be confirmed, unfortuantely, no improvement in dust pickup could be observed. Probably since the surface developed its maximum cure by chemical means (peroxide) and no further cure could be obtained by radiation.

6.5   Solution Coatings. Modification of existing surface quality was attempted through application coating to provide a harder, less sticky (less dust pickup) surface. Some coatings were applied prior to electron beam irradiation in an attempt to either cure the coating (Elvax 150) or improve coating-substrate adhesion (Acryloid AT-56).

The following materials were investigated:

Commercial Name	Composition
Elvax 150	EVA polymer tried in 15% toluene solution.
Acryloid AT-50	Thermoset acrylic supplied as 50% solution.
Acryloid AT-56 Cymel-325	A 55% solution made into a thermoset acrylic composition.
Acryloid A-10	Thermoplastic MMA; 30% in cellosolve acetate.
Acryloid B-50	Thermoplastic MMA copolymer; 45% solution in toluene.
PPG-5 (CSL)	Believed to be PPG 77-5, an alkyd-urethane supplied by CSL and used as a 1:1:1 solution PPG-5/Toluene/Acetone. According to PPG the product is 47% in mineral spirits; thus, 1:1:1 ratio yields a 16% solution.

The following acrylic solutions were prepared from 100% solution grade resin:

Acryloid A-11	31.5 gr.	Acryloid A-11	52.5 gr.
Acryloid B-44	68.2 gr.	Acryloid B-82	52.5 gr.
Tenite 472	5.2 gr.	Toluene	195.0 gr.
Toluene	195.0 gr.		
MEK	28.1 gr.		
Solids: 32%		Solids: 35%	

Suppliers:

Elvax	DuPont
Acryloid	Rohm & Haas
Cymel	American Cyanamid
PPG-5	Pittsburgh Plate Glass
Tenite	Eastman

For initial evaluation, coatings were cast on approximately 1" wide strips of cured standard compound 8247-1: 6150C with 0.5 parts Antioxidant 330. Coatings were approximately 1 mil thick. Coatings were allowed to air dry, then were baked at 300°F for 15 minutes.

All strips were evaluated as follows:

1) Surface quality judged subjectively in regard to ability to resist dirt pickup;

2) Resistance to cracking on flexure - the brittleness of the film was evaluated by flexing the sample and observing the film for cracks;

3) Adhesion - in the above test (2) any signs of delamination were noted. The coating was subjected to a crosshatch test where a crosshatch pattern is cut in the coating with a razor and a piece of Scotch tape is applied over the pattern. The tape is then removed and the number of squares seen to delaminate is recorded.

From the above tested materials, the urethane coating received from CSL (PPG-5) appeared to be the best of the coatings examined. Adhesion and flexibility are excellent and surface improvement is marked.

Consequently, and as requested by CSL, the lens used in some of the two-piece masks submitted to CSL (five complete masks) were coated with PPG-5.

The "as received" PPG-5 material (supplied by CSL) was diluted to an approximate concentration of 7% solids. This was done by adding a 50/50 blend of acetone and toluene to the PPG-5 material.

The lens were immersed in a beaker containing this diluted solution of PPG-5 and pulled out of the solution vertically, at a speed of half in/ minute.

The coated lens were cured in an oven. The oven temperature was 250°F. The curing time was 2 hours.

7. CYCLOHEXYLAMINE AND MEK PERMEABILITY

Permeability tests on both cyclohexylamine and MEK were performed on 100 mil thick sheets. The exposed areas of the polymer sheets (uncured or cured) varied from 95 to 140 square centimeters. The measured values were then converted to express micorgrams per square centimeter.

The results of these tests are shown in table 6. Included in this table are test results covering the first twelve months of our contract effort, for comparison.

We point out that it was agreed that candidates which passed more than 1.25 micrograms of cyclohexylamine or more than 4.0 micrograms of MEK per square centimeter in a 360-minute period were to be eliminated from the study.

There are indications that the 1.25- and 4.0-microgram specifications, respectively, are too severe and probably eliminate some otherwise useful candidates.

8. CHEMICAL RESISTANCE

After the screening tests (approximately after the fifteenth month of this contract, the following polymer vulcanizates seemed to offer the desired combined all-around properties:

> Nordel 1320
> Royalene 521
> Elvax 150
> Vynathene EY 903
> LR3-463
> Pellethane 2363-80A

These vulcanizates were now examined for chemical resistance. Results of these tests are shown in table 7.

9. TENSILE PROPERTIES AND HARDNESS

9.1 Elastomer Blends (EPDM/EVA). Blends have some inherent special characteristics. Polymers are usually not miscible, and blends consist of microdispersions of one in the other or of intermingled microregions of both - often having dimensions around 0.1 to 1.5 microns. When fillers are mixed into such a blend, a situation may develop in which the filler is unevenly distributed over the two different phases, thereby affecting the compound properties.

With these considerations in mind, efforts were made to take advantage of the combined properties of EPDM and EVA polymers. Results of our earlier work indicated that some of the ethylene/vinyl acetate (EVA) copolymers combined with EPDM could become candidates. On this basis, EVA/EPDM cuts were compounded with silica and cured with Vul-Cup R. Also, uncured and cured EVA polymers were examined to see what physical properties could be gained by compounding EPDM with EVA.

Table 6. Cyclohexylamine and MEK Permeability Tests

Trade Name	Polymer		Permeability [a] (microgram/cm^2)	
	Type	State	Cyclohexyl-amine	MEK
Chemplex 3000	EVA	Uncured	0.21	>11.2
Chemplex 3311	EVA	Uncured	0.20	> 8.0
Vynathene EY 903	EVA	Uncured	0	> 8.0
Vynathene EY 903	EVA	Vul-Cup cured	0	3.52
Vynathene EY 903 + Nordel 1320	EVA/EPDM 30/70	Vul-Cup cured	0	0.23
Elvax 150	EVA	Uncured	1.54	>11.2
Kel-F 6060	Fluorinated	Uncured	1.25 [b]	> 8.0
Kel-F 6061	Fluorinated	Uncured	1.25 [b]	> 8.0
Pellethane 2363-80A	Urethane	Uncured	1.05	1.80
LR3-463	Urethane	Cured	Passed [c]	Passed [c]
Nordel 1320	EPDM	Uncured	0.28	0
Nordel 1320	EPDM	Di-Cup cured	0	3.24
Nordel 1040	EPDM	Uncured	0	>8.0
Nordel 1040	EPDM	Di-Cup cured	0	0
Royalene 521	EPDM	Uncured	5.25	>11.2
Royalene 521	EPDM	Di-Cup cured	0	0
Royalene 521	EPDM	Vul-Cup cured	0.72	2.10
Vistalon 404	EPDM	Uncured	0	> 8.0
Vistalon 404	EPDM	Di-Cup cured	0.47	> 8.0

(a) Thickness of specimen: 100 mils.
(b) Considerably higher amount than 1.25 micrograms.
(c) As tested by Du Pont and Edgewood, respectively.

Table 7. Chemical Resistance Tests

Reference Number	Composition (a)	Testing Media					
		Gasoline	Diesel Fuel	Ethanol (Synasol)	I	II	LSA
A6976	Vynathene 903 - uncured	Cr. & Bl.	Cr. & Bl.	Passed	Passed[b]	Eats away surface	Sl. Hz.[c]
A6975	Vynathene 903 - cured	Sl. Yl.	Passed	Sl. Yl.	Passed	Passed	Sl. Hz.[c]
A6991C	Vynathene 903/Nordel 1320, 50/50 - cured	Passed	Attacked[c]	Passed	Attacked[c]	Passed	Attacked[c]
A6992	Vynathene 903/Nordel 1320, 30/70 - cured	Passed	Attacked[c]	Passed	Sl. Hz.	Passed	Sl. Hz.
A6996	Vynathene 903 - cured, with TAC activator	Passed	Passed	Passed	Passed	Sl. Hz.	Very Hz.
A6150C	Nordel 1320 - cured	Passed	Attacked[c]	Passed	Sl. Hz.	Passed	Sl. Hz.
A6974	Elvax 150 - uncured	Cr. & Bl.	Became slimy	Passed	Sl. Hz.	Cr. & Bl.	Very Hz. & Cr.
A6973 or A7717	Elvax 150 - cured	Passed	Passed	Passed	Passed	Cr. & Sl. Hz.	Passed[c]
A6988C	Elvax 150/Royalene 521 50/50 - cured	Passed	Sl. Hz.	Passed	Sl. Hz.	Very Hz.	Passed
A6989	Elvax 150/Royalene 521 30/70 - cured	Very Hz.	Very Hz.	Attacked	Passed	Attacked	Sl. Hz.
2363-80A	Upjohn urethane - cured	Passed	Sl. Hz.	Passed	Passed	Passed	Sl. Hz.
LR3-463	DuPont urethane - cured	Passed	Passed[d]	Attacked[c]	Passed[d]	Passed	Passed

(a) Cured with Vul-Cup R, 350°F/15 minutes; EPDM fraction contains 3 parts silica/100 parts EPDM.
(b) Strong odor emitted.   (c) Chemical leaves ring following blotting.
(d) Optical clarity seemed to improve in contact with this chemical.

CODE: Cr = Crazed; Bl = Blistered; Sl = Slightly; Yl = Yellowed; Hz = Hazy

33

Table 8. EPDM/EVA Compositions – Physical Properties

Reference Number	Composition (a)	Physical Properties			
		Tensile Strength (psi)	Modulus at 100% (psi)	Ultimate Elongation (%)	Hardness (Shore A)
A6976	Vynathene 903 – uncured	1350	150	860	52
A6975	Vynathene 903 – cured	491	187	290	56
A6991C	Vynathene 903/Nordel 1320 50/50 – cured	438	176	340	56
A6992 [b]	Vynathene 903/Nordel 1320 30/70 – cured	238	167	210	55
A6996 [b]	Vynathene 903 – cured, with TAC activator	538	210	330	56
A6974	Elvax 150 – uncured	677	272	940	68
A6973	Elvax 150 – cured	1107	330	390	72
A6983	Elvax 150/Nordel 1320, 50/50 – cured	575	240	370	63
A6988C	Elvax 150/Royalene 521, 50/50 – cured	605	214	410	60
A6985	Elvax 150/Nordel 1320, 30/70 – cured	370	198	290	58
A6989	Elvax 150/Royalene 1320, 30/70 – cured	402	181	390	55
A6150C [b]	Nordel 1320 – cured	149	146	110	55

(a) Cured with Vul-Cup R at 350°F for 15 minutes; EPDM fraction contains 3 parts silica/100 parts EPDM.

(b) Became a final candidate.

The EVA polymers examined were:

Vynathene EY 903 (U.S.I.)
Elvax 150 (DuPont)

To learn more about these polymers, the EVA materials were evaluated in both the uncured and cured forms. With the cured blends, ratios of 30/70 and 50/50 EVA/EPDM were tried. No effort was made to evaluate higher ratios of EVA since our experience indicates that higher ratios impair optical clarity and cause high hardness of the vulcanizate. The results of these tests are shown in table 8.

Normally, the tensile strength of an elastomer can be increased by curing. It was surprising to learn that the attempt to cure Vynathene 903 with Vul-Cup R yielded a tensile strength significantly inferior to that of the uncured specimen (see table 8). We have no explanation for this. A second attempt was made to cure Vynathene - this time with the help of triallyl cyanurate (TAC) - see A6996. This activator helped to take advantage of the peroxide curing system; however, the resultant tensile strength was still significantly inferior to that ot the uncured stock.

Cuts of Vynathene 903 and Nordel 1320 yielded physical properties between those of uncured Vynathene and cured Nordel, respectively. Thus the physical properties of Nordel could be upgraded.

From our earlier work, Elvax 150 - actually a hot-melt adhesive raw material - appeared promising. We, therefore, tried taking advantage of the combined properties of Elvax 150 and EPDM, using the peroxide-cured form. As we expected Elvax cured with a peroxide system yielded improved physical properties. The improvement observed in conjunction with Elvax/EPDM vulcanizates is proportional with the Elvax/EPDM ratio. The hardness, however, also increases with the ratio of Elvax (a disadvantage for our project). The 30/70 Elvax/EPDM ratio offers the best combination of physical properties. Stepwise cures versus a one-step cure do not bring any significant change in physical properties - see table 9.

Table 9. Stepwise Curing of an Elvax 150/Nordel 1320
Composition (Elvax/Nordel Ratio: 50/50)

Cure (°F/Minutes)		Tensile Strength (psi)	Modulus at 100% (psi)	Ultimate Elongation (%)
Precure	Final Cure			
-	350/15	575	240	370
300/5	370/10	531	236	340
270/5	370/10	601	242	360

9.2   Radiation-Cured EVA. Peroxide-cured Elvax 150 compounds had attractive optical properties ("window-glass" effect). Also, the physical properties of these vulcanizates were quite satisfactory. On the other hand, the molding and curing of the Elvax compounds presented a real problem.

The possibility occurred that Elvax 150 could be cured by radiation to obtain the desired physical properties. If so, the molding procedure could be simplified, since the Elvax could be molded below its melting point (no need for the higher temperature to activate the peroxide). Thus, the sticking problem could be eliminated. Also, the surface of the cured Elvax should be smoother than that obtained by peroxide cure, as obvious flow marks can be seen on a compression-molded, peroxide-cured Elvax specimen.

Elvax 150 was compression-molded below its melting point into 6" x 6" plaques, 75 and 100 mils thick; these plaques were radiation-cured by a dosage of 2.5 megarads. The radiation-cured Elvax 150 displayed excellent tensile strength and elongation, with an unusual balance of tensile and elongation. Physical properties of this material are shown in table 10.

Table 10.   Elvax 150 - Curing Method/
Physical Properties

Curing Method	Reference Number	Tensile Strength (psi)	Elongation (%)	Modulus at 100% Elongation (psi)
Uncured	A6974	677	940	272
Peroxide	A6973	1107	390	330
Radiation	A7739	1319	685	310

9.3   Conjugated Diene Butyl (CDB). A one-gallon sample of experimental product was obtained from Exxon; this was a styrene-butyl rubber solution consisting of 40 percent CDB and 60 percent styrene.

The following starting formula was made first into a mill batch and was later prepared by mixing the ingredients in an internal mixer (Brabender):

	Parts by Weight
CBD in styrene (as supplied by Exxon)	160.0
t- Butyl perbenzoate	1.6
Irganox 1010 (phenolic antioxidant)	0.2
DSTDP	0.5

Six batches were made, but each batch behaved differently, depending on the amount of styrene which evaporated during compounding. In other words, it was not possible to duplicate product properties.

The best product we obtained was made by compression-molding at 230°F for 60 minutes. Another vulcanizate having fair optical clarity was made by stepwise curing at 200°F for 5 minutes, followed by a 49-minute period at 250°F.

It is quite clear that here we are faced with a new technology (graft curing) rather than with a new product, and many other parameters (and co-monomers) should be investigated to explore eventual merits for our project.

9.4   Urethanes. Two polymers were considered for our program: Pellethane 2363-80A from Upjohn, and an experimental polyurethane from DuPont referred to as LR3-463.

Both urethanes passed the optical clarity specifications, and it was learned from previous work that these polymers pass the MEK and cyclohexylamine tests. Therefore, they were tested for tensile and elongation. Results of these tests are shown in Table 11.

Table 11. Polyurethanes –
Physical Properties

Reference Number (Designation)	Tensile Strength (psi)	Modulus at 100% (psi)	Ultimate Elongation (%)
Pellethane 2363-80A	8773	1919	452
DuPont LR3-463	4147	200[a]	504
(a) As reported by DuPont			

Both urethanes considerably exceeded the required tensile/elongation properties, but Pellethane 2363-80A displayed a Shore A hardness in excess of 90 (Pellethane 2363-80A also displayed a very high compression set). We intended to modify this polymer with the aid of a soft urethane composition, Isonol 93, suggested by Upjohn. But we were never able to obtain a sample of this material. As a result, Pellethane 2363-80A phased out of our program. DuPont LR3-463 was retained for further testing.

10.   OPTICAL UNIFORMITY AND OPTICAL CLARITY AFTER ABRASION

When this phase of the program was reached, the number of candidates had been reduced to five materials:

Reference Number	Polymer Composition
A6150C	100% Nordel 1320
A6992	Nordel 1320/Vynathene CY 903, 70/30 blend
A6696	100% Vinathene EY 903
A7717	100% Elvax 150
LR3-463	Polyurethane as made by DuPont

The exact compositions of these materials are shown in a later table (p. 44).

Optical uniformity of the candidate lens materials was tested in accordance with ASTM D637 (see Testing Methods - Part 4). Results of these tests are shown in table 12.

Table 12. Optical Uniformity

Candidate Number	Displacement Factor		Image Movement (Type of Movement)	Pattern[a] Distance
	Horizontal	Vertical		
A6150C	2.5	5.0	Single shift	15
A6992	30.0	20.0	Single shift	15
A6696	30.0	2.5	Single shift	15
A7717	5.0	20.0	Frequent	10
LR3-463	200.0	30.0	Irregular and wavy	5

For abrasion tests, the specimens were first treated in accordance with Method 1092 of Federal Standard 406 using CS 10F calibrase wheels for 50 cycles under a 500-gram load. The specimens were then examined for optical clarity. The results of these tests are shown in table 13.

Table 13. Abrasion Resistance of Candidates
as Measured by Optical Clarity

Reference Number:	6150C	6992	6996	7717	LR3-463
PROPERTIES					
Optical clarity					
Haze, % - Original	5	8	9	9	
- After abrasion	22	11	21	25	-
Light transmission, %					
- Original	83	82	77	87	(a)
- After abrasion	73	78	73	72	-

(a) Measured by DuPont and CSL respectively.

11.   COMPRESSION SET OF EARLY CANDIDATES

Both polyurethanes, Pellethane 2363-80A and LR3-463, failed badly on compression set testing at 100°C (212°F), with values of 65 percent and 67 percent, respectively. The LR3-463 was examined at 70°C as well, with a resultant compression set value of 44 percent.

The other candidates, based on EPDM, EVA, and EPDM/EVA blends, respectively, displayed very low compression set values. It is interesting to note that all three candidates - A6992, A6996, and A7717 (Nordel 1320/Vynathene 903 blend Vynathene 903, and Elvax 150, respectively) showed an improved compression set at 100°C. It would appear that the exposure to 100°C (versus 70°C) might help to establish an improved state of cure. Results of these tests are tabulated in table 14.

Table 14.   Compression Set of Lens Candidates

	6150C	6992	6995	7717	LR3-463
Compression set, % at 70°C	--	7	9	12	44
at 100°C	13	5	2	9	67

12.   FLEXIBILITY

Flexibility tests were performed in accordance with Test Method EAQ 37. Sample size was 3.5" x 0.5" x 100 mils.

The Nordel 1320 vulcanizate, 6150C, retained 100 percent flexibility at -25°F. This was not surprising since earlier tests indicated extremely low (below - 145°F) brittle temperatures for EPDM vulcanizates. The EVA candidates retained only 10-15 percent flexibility at -25°F, while the EPDM/EVA blend displayed a flexibility proportional to the EPDM/EVA ratio.

The results of these tests are shown in table 15.

Table 15.   Flexibility of Early Candidates

	6150C	6992	6996	7717	LR3-463
Flexibility, % retained at -25°C	100	63	10	15	(a)

(a)   Measured by DuPont and CSL, respectively.

13. ANTIOXIDANTS

Peroxide-cured compounds can be improved through the use of antioxidants. While superior compound properties may be obtained by this means, most of the powerful antioxidants - particularly those which can serve also as antiozonants - can function as "free-radical scavengers" and consume peroxide, thus disturbing the peroxide curing process. The net effect is a significant reduction in active levels of the peroxide. This is the reason why we investigated antioxidant only in a very superficial manner.

It has been confirmed (see earlier parts of this report) that 0.5 parts of Antioxidant 330 are sufficient in our Nordel 1320 formulation (6150C) to yield proper balance of aging and physical properties. Antioxidant 330, however, caused a somewhat yellowish color (not disturbing to optical clarity).

In a series of tests, various antioxidants were tried to replace Antioxidant 330. These antioxidants and/or antioxidant combinations were examined at the earlier established 0.5 parts level.

The vulcanizates (cure: 15 minutes at 350°F) were aged overnight (16 hours) at 150°C. The samples were examined for color and tack (dust pickup) of the surface. These aged samples were compared with the unaged samples. The aged samples and unaged samples were rated according to the following code:

1. Outstanding color and clarity.
2. Good color/clarity.
3. Color formation significant/haze becoming a problem.
4. Strong color formation/haze.
5. Strong evidence of degradation color and haze.

The unaged samples were also examined for state of cure by determining the gel-content of vulcanizates. Results are shown in table 16.

The following additional information is of interest:

Samples -1 and -2 appeared to be well protected in spite of brown color. Unaged samples were dark in color because of the antioxidant. Samples -5 and -10 showed streaks of some gummy material; probably indicating poor peroxide dispersion resulting in uncured areas; -7 and -11 were rated best with -7 slightly lighter in color).

These tests confirmed that phenolic antioxidants work well with the Nordel 1320/Vulcup R system. The two best samples were:

0.5 parts Antioxidant 330
0.25 parts Irganox 1010
0.25 parts Irganox MD 1024

The hydroquinoline antioxidants work well but impart a dark color to the stock initially. Clarity, however, is not affected.

Table 16. Study of Antioxidants in EPDM -6150C

Ref. No.	Antioxidant	Composition of Antioxidant	% gel	Heat-aged	Unaged
A1QQ10-Q	Control	- - -	98.16	1	3.5
-1	Agerite MA	Polymeric hydroquinoline	98.09	3	3
-2	Agerite Resin D	Polymeric hydroquinoline	97.58	3	3
-3	Vanox ZMTI Methyl Niclate	Zn mercaptotolylimidazole Ni dimethyldithiocarbamate	97.47	3.5	3
-4	Vanox MTI	Mercaptotolylimidazole	96.51	3	3
-5	Naugard P	Organic phosphite	96.85	5	3
-6	Naugard P DLTDP	Organic phosphite Dilaurylthiodiproprionate	91.08	2	2
-7	Irganox 1010 Irganox MD 1024	Hindred phenol Phenolic metal-deactivator	97.66	2.5	2
-8	Santowhite Naugard P DSTDP	Hindred cresol Organic phosphite Distearylthiodipropionate	93.90	2.5	3
-9	DLTDP Topanol CA	Distearylthiodipropionate Hindred phenol	96.98	2.0	2.5
-10	Irganox 1076	Hindred phenol/propionate	97.42	4.0	2
-11	Antioxidant 330	Hindred phenol	97.67	2	2

In view of these findings, the Irganox 1010/Irganox MD 1024 antioxidant combination was examined as a potential replacement for Antioxidant 330 to improve color.

Unfortunately, it was concluded that the Irganox 1010/Irganox 1024 combination is not sufficiently st?ble under our regular molding temperature (350^OF). Bubbles developed in the compression-molded vulcanizates. This could be improved on by transfer-molding the compound but not sufficiently to consider this antioxidant combination for the final candidate material(s). As a result, 0.5 parts Antioxidant 330 became our candidate 6150C modification.

14.   LONG-TERM STORAGE TESTS

The candidates were subjected to a nine-week storage test under desert, tropic, and arctic conditions (160^OF, 4% RH; 113^OF, 80% RH: and -65%, respectively), after which exposure the vulcanizates so aged were tested for tensile and elongation properties. The results of these tests are tabulated in a later table (p. 44).

In summary, it was found that:

. No severe changes of tensile properties were noticed in connection with the arctic condition aging tests. The EPDM, EVA, and EPDM/EVA vulcanizates retained their tensile and elongation, or slightly increased in tensile and/or elongation. LR3-463, the polyurethane candidate, displayed a slight loss of properties.

. The tropic-aged EVA vulcanizates (6996 and 7717) showed significant loss in tensile and elongation, as did LR3-463.

. The desert-aged Nordel 1320 and Vynathene EY 903 vulcanizates as well as the vulcanizate made of the blend of these two polymers (6150C, 6996, and 6992, respectively), lost some 40 percent of their tensile strength and elongation properties. Interestingly enough, the Elvax vulcanizate (7717) and the polyurethane candidate (LR3-463) developed an increased tensile strength and elongation during this nine-week exposure.

We repeated some of these experiments to see if desert-condition aging of the Nordel and Vynathene candidates could be improved. We used Antioxidant 330 from Ethyl Corporation (chemically 1,3,5-trimethyl-2,4,6-tris/3,5-di-tert-butyl-4-hydroxybenzyl/benzene). This phenolic antioxidant is not easy to sublime (unlike other phenolic antioxidants), and it was therefore assumed that such an antioxidant would be retained by the compound during vulcanization.

A very significant improvement in physical properties and aging could be obtained by the use of Antioxidant 330.

Antioxidant 330 at 1.0 part concentration imparts an undesirable level of yellow color. In our study it was established that 0.5 parts of Antioxidant 330 in 6150C yields a vulcanizate with good balance of physical properties, optical clarity, with less yellow color, and a somewhat improved surface. This vulcanizate, 8247-1, became our new candidate material.

In order to learn more about the long-term aging of this vulcanizate, and some other modifications, the following materials were subjected to heat aging test at 250°F to investigate heat stability, color formation, and loss of physical properties:

6150C	Control
8247-1	6150C with 0.5 phr Antioxidant 330
8238	6150C with 1.0 phr Antioxidant 330
10031-8	8247-1 irradiated with 2.5 Mrad

The following results were obtained after 45 hours of exposure (table 17).

Table 17. Accelerated Heat-Aging of
Nordel 1320 Vulcanizates

Reference	Tensile psi	Elongation %	Appearance
6150C	199	178	Slightly yellow, very gummy and sticky on side exposed to hot air.
8247-1	219	203	Noticeably yellow, no gummy surface.
8238	262	338	Very noticeably yellow, no gummy surface.
10031-8	214	185	Noticeably yellow - no gumminess, no more yellow than 8247-1.

The following conclusions can be made:

At 250°F, oxidative attack on surface of unprotected material is severe after two days. Antioxidant 330 is very useful in preventing this, but color formation does develop under this type of heat aging.

Color formation is not as significant in this unprotected material, but surface quality suffers.

Radiation curing does not appear to affect the heat stability of the vulcanizate. The irradiated vulcanizate appears to behave similar to the corresponding control (8247-1) regarding color formation and surface quality.

15. SELECTION OF FINAL CANDIDATE

It will be noted that a systematic and progressive development and screening of lens candidates took place during the second twelve-month period (modification) of this contract. A part of this program was built around the knowledge and findings accumulated during the first twelve-month period of the contract (see Sections Polymers and Curing Systems, Preliminary Screening Tests and Results, and Cyclohexylamine and MEK Permeability).

Selection of final candidates was based on all-around properties and performance. This selection led to 6150C (Nordel 1320 vulcanizate): 6992 (covulcanized Nordel 1320/Vynathene CY 903); 6996 (Vynathene EY 903 vulcanizate); 7717 (Elvax 150 vulcanizate); and LR3-463 (a polyurethane vulcanizate). Improved versions of 6150, 6992, and 6996 were obtained by modifying these compounds with a phenolic antioxidant.

The Elvax 150 vulcanizate (7717) displayed very poor low-temperature flexibility.

The DuPont urethane polymer, LR3-463, while also causing molding problems, displayed high compression set and poor low-temperature flexibility. Also, it has been found that all LR3-463 vulcanizates developed high haze in storage (2- to 3-month storage time). This haze was difficult to remove, as it was not a surface phenomenon only. DuPont confirmed that this change does take place and that it is a result of slow crystallization. According to Du-Pont, this could be improved on by using a polyether starting material in making the LR3-463 polymer (specifically, tetraethylene glycol).

The compositions and some of the critical properties of these candidate materials are presented in table 18.

Our basic intermediate Nordel 1320 candidate referred to as 6150C, had the following formulation:

	Parts by Weight
Nordel 1320	100.0
Cabosil MS-7	3.0
Vul-Cup R	1.5

Cure: 15 minutes at 350°F

Our final candidate became the formula with 0.5 parts of Antioxidant 330. This final lens candidate has the designation 8247-1. This vulcanizate has excellent aging properties, and slightly higher tensile values than 6150C. It has a higher state of cure than 6150C, and, therefore, displays somewhat less dust pickup than 6150C. To maintain maximum optical clarity, no mold-release agent is used for vulcanization.

Table 18. Critical Properties of Lens Candidates

Reference Number:	6150C	8238	6992	8239	6996	8240	7717	LR3-463
. COMPOSITION (Parts by Wt)								
Polymer –								
Nordel 1320	100.0	100.0	70.0	70.0	–	–	–	–
Vynathene EY 903	–	–	30.0	30.0	100.0	100.0	–	–
Elvax 150	–	–	–	–	–	–	100.0	–
LR3-463 (a)	–	–	–	–	–	–	–	100.0
Additives –								
Cabosil MS-7	3.0	3.0	3.0	3.0	–	–	–	–
SR-350	–	–	–	–	–	–	2.0	–
Triallyl cyanurate	–	–	–	–	1.0	1.0	–	–
Vul-Cup R	1.5	1.5	1.5	1.5	1.0	1.0	1.5	–
Antioxidant 330	–	1.0	–	1.0	–	1.0	–	–
Cure – minutes/°F	15/350	15/350	15/350	15/350	15/350	15/350	15/350	10/302
. PROPERTIES								
Optical clarity								
Haze, % – Original	5[b]	4[c]	8[b]	15[c]	9[b]	5[c]	9[b]	(d)
– After abrasion	22	–	11	–	21	–	25	–
Light transmission, %								
– Original	83[b]	87[c]	82[b]	9[c]	77[b]	13[c]	87[b]	(d)
– After abrasion	73	–	78	–	73	–	72	–
Tensile, psi								
Original	181	198	238	525	538	1591	1342	4147
Desert-aged	112	183	136	508	330	1637	1876	7043
Tropic-aged	171	–	276	–	290	–	891	2819
Arctic-aged	180	–	317	–	664	–	1994	3232
Elongation, %								
Original	125	387	210	489	477	494	377	504
Desert-aged	76	272	139	438	292	476	409	544
Tropic-aged	94	–	203	–	197	–	330	469
Arctic-aged	128	–	250	–	309	–	404	490
Tear resistance, lb/inch	32	–	54	–	88	–	149	264
Hardness, Shore A	55	–	55	–	56	–	–	–
Compression set, %								
At 70°C	–	–	7	–	9	–	12	44
At 100°C	13	–	5	–	2	–	9	67
Flexibility, % retained at -25°C	100	–	63	–	10	–	15	(d)

(a) As compounded by Du Pont.
(b) Average
(c) Based on one test only; all three vulcanizates had a yellowish color.
(d) Measured by Du Pont and Edgewood, respectively.

16.   NORDEL VARIATIONS

As mentioned earlier, 8247-1 vulcanizates made during the last months tended to yield a surface with an "orange peel" affect. Further investigation into this (laboratory batches 10048, 10049 10901-A and -B, 10902-1 and -2, and 10903) by changing raw material lot numbers and drying the silica prior to compounding, clearly indicate a change in Nordel 1320.

Striking was to discover extreme color differences between recent Nordel 1320 shipment. Most significant was a 20 pound sample shipment which arrived in October 1979. This shipment arrived in four 5 pound boxes. The sample carrying lot number H9181725 was the most water-clear Nordel 1320 we ever received, while the one carrying lot number H2164096 was the darkest Nordel we ever worked with (intense yellow).

Fortunately, the optical clarity of the lens vulcanizates does not suffer from these quality variations. However, the appearance of the lens vulcanizates does.

Optical clarity results obtained on various Nordel 1320 vulcanizates are shown in table 19.

It should be pointed out that Nordel 1320 vulcanizates made with Antioxidant 330 cured with Vulcup R do tend to yield non-uniform tensile values. This was first suspected as the cause of the "orange peel" affect.

It is difficult to obtain a uniform dispersion of the Antioxidant 330/ Vulcup R combination in a low Mooney viscosity EPDM like Nordel 1320 (Mooney = 20).

Since the antioxidant 330/Vulcup R system yields a high state of cure, which improves the surface characteristics of the vulcanizate (less dust pickup), attempts have been made to masterbatch these ingredients in a high Mooney EPDM (for better dispersion) first, later diluting the masterbatch with Nordel 1320.

Two such higher Mooney EPDM polymers have been tried: Nordel 1040 and Royalene 521. The former (according to DuPont) is made with the same stabilizing and additive system as Nordel 1320. Therefore, it should be quite compatible with Nordel 1320. Royalene 521, on the other hand, was for some time one of the approved candidates of Edgewood.

The following masterbatch formulation was used:

High Mooney EPDM	100.0 parts
Cabosil MS-7	15.0 parts
Antioxidant	2.5 parts
Vulcup R	7.5 parts

Table 19. Optical Clarity of Nordel 1320 Vulcanizates

Composition of Nordel 1320 Compound[*]						Curing Cycle (°F/min)	Light Trans- mission (%)	Haze (%)
Acetone Extracted	Di- Cup	Vul- Cup	Sil- ica	SR 350	Mold Release Agent			
No	2.5	–	–	–	Yes	350/15	72.5	12.8
No	2.5	–	–	–	Yes	350/5+ 370/10	85/3	5.3
No	2.5	–	3.0	–	Yes	350/15	82.4	9.3
Yes	2.5	–	–	–	Yes	350/15	82.8	19.9
No	–	1.5	3.0	–	No	350/15	90.0	2.2
No	–	1.5	3.0	2.0	None	350/15	86.6	3.9
No	2.5	–	3.0	2.0	No	350/15	70.2	11.5
Yes	2.5	–	3.0	2.0	Yes	350/5+ 370/10	85.3	7.0
No	–	1.5	3.0	–	Yes	350/15	88.0	5.2
No	–	1.5	3.0	2.0	None	350/15	86.0	3.9
No	–	1.5	6.0	4.0	None	350/15	79.2	12.3
No	–	1.5	6.0	–	None	350/15	–	–
No	–	1.5	3.0	4.0	None	350/15	82.5	6.5
No	–	1.5	–	2.0	None	350/15	71.4	42.3
No	–	1.5	3.0	4.0	None	300/5+ 370/10	77.4	6.4
No	–	1.5	6.0	4.0	None	300/5+ 370/10	74.6	9.6
Yes	–	1.5	6.0	–	None	300/5+ 370/10	–	–
Yes	–	1.5	6.0	4.0	None	300/5+ 370/10	76.8	7.7

* Parts per 100 parts of Nordel 1320

47

Vulcanizates were made from 80 parts Nordel 1320 and 20 parts of master-batch to form the standard EPDM/silica/Vulcup R ratio (similar to candidate 6150C). The 80:20 ratio yields the earlier established 0.5 parts concentration of the antioxidant. Two antioxidants, Antioxidant 330, and the 50/50 Irganox 1010/Irganox MD 1024, were evaluated in these masterbatched compositions. The vulcanizates developed high haze: 14.6% and 14.8% with the Antioxidant 330 and Irganox combination respectively. Increased haze was observed after some weeks of storage. The high Mooney Nordel seems to crystallize. This crystallization, in turn, is responsible for the poor optical clarity of the vulcanizate.

Royalene 521 does not follow the same pattern. Vulcanizates made with Royalene 521 masterbatch, in 80/20 masterbatch/Nordel 1320 ratio, displayed good optical clarity. Haze was 4.6% when Antioxidant 330 was used, and 5.3% with the Irganox blend. No significant tensile improvement could be realized with the help of Royalene 521 masterbatch. From this, and from earlier work (done with EVA polymers), it seems 20% is not a high enough ratio to upgrade physical properties of Nordel 1320 vulcanizates with other polymers.

Following along the guidelines set by DuPont for clear EPDM (Article: Transparent Nordel Formulations) several additional methods of upgrading Nordel 1320 were tried. Nordel 1560 and Nordel 1320 were tried in our 6150C type for-mulation. Molded plaques made with Nordel 1560 were very hazy – as actually expected of a high Mooney EPDM. The degree of transparency obtained by DuPont is questionable.

Nordel 2522 handles much easier on the mill without crumbling. Because of this, Nordel 2522 was thought to be a candidate for masterbatching ingredients if further dispersion problems with the Vulcup R/Antioxidant 330 system were en-countered.

Unfortunately, when Nordel 1320 is fully replaced with Nordel 2522, the optical clarity of the final vulcanizate suffers. Also, the improvements in physical properties of the vulcanizate (versus Nordel 1320) are marginal. Im-provements in physical properties could be obtained when the Vulcup R curing system was changed to DiCup. DiCup cures, however, as pointed out in the early reports of this project – have a very objectionable odor.

In view of these findings, no more attention was devoted to Nordel 2522.

17.   FACEBLANK LENS MATERIAL ADHESION

The following commercial grades of adhesives were examined to determine bonding value and to develop techniques for bonding the lens material to the natural rubber faceblank material:

Trade Names	Suppliers
Bostik 2032	Bostik Division, USM Corp.
Boscodur 23	Bostik Division, USM Corp.
Chem-Fast 20	Devcon Corporation
Super Bonder 414	Loctite Corporation
Eastman 910	Eastman Chemical Products, Inc.
Chemlok 7002	Hughson Chemicals, Lord Corp.
Chemlok 7202	Hughson Chemical, Lord Corp.
Chemlok 305-1	Hughson Chemicals, Lord Corp.
Chemlok 305-2	Hughson Chemicals, Lord Corp.

Slabs of the faceblank material and plaques of the candidates were made into 1" x 2" strips. The surfaces of both strips (faceblank and candidate material) were cleaned with acetone and one drop of adhesive applied to the first 1/4 inch of the strips using a cotton roll. The overlapping 1/4 inch portions of the two strips were pressed for 5 seconds. A weight was kept on the overlap area while the adhesive film was drying. After 24 hours the specimens were pulled by hand to examine the strength of the adhesive bond.

As a result of these screening tests, two commercial grades of adhesives (Eastman 910 and Super Bonder 414) showed promise and were retained for further work. Super Bonder 414 displayed a bond strength of 47 lb/inch and Eastman 910 a strength of 46 lb/inch. These results were obtained on vulcanized specimens of 6150C. Super Bonder 414, because of its higher optical clarity was later tested on the antioxidant modified vulcanizate 8247-1. Results are reported below.

Bond Strength Obtained on 8247-1 Vulcanizates With Super Bonder 414

Surface Preparation	Bond Strength psi
No surface preparation	12
Acetone wash - both surfaces	11
Acetone wash - sanded both surfaces	15
Isopropanol wash - both surfaces	10
Isopropanol wash - sanded both surfaces	13
PPG-5 coating on 8247-1 - NR faceblank washed with acetone	17*

*The clear urethane section broke; no peel.

Aging of faceblank/lens material adhesion studied by gluing one inch wide strips of the faceblank and 8247-1 vulcanizates with Loctite Super-Bonder 414 in a 1/2" overlap area. The following physical properties were measured after aging these specimens at various conditions:

49

	Type of Aging		
	Tropic	Desert	Arctic
Aged adhesives bond, psi	23.5	14.9	14.2
Aged/glued lens material			
Tensile strength, psi	140	163	--
Elongation, %	220	168	--

To double check the adhesion values the following test was performed:

A molded faceblank was cut into one inch wide strips with groove endings on one side. A compression molded 100 mil thick 8247-1 lens material vulcanizate was cut into one inch wide strips. Then, the lens material strips were glued into the grooves of the faceblank strips. This way, the freshly glued lens material edge adhered to three surfaces of the groove.

The glued specimens were pull-tested after 24 hours drying, and the force necessary to separate the lens material from the faceblank groove was recorded.

Two practically identical, but in set-up time slightly different Loctite adhesives were tried: Loctite Super-Bonder 414 and 415. The following results were obtained:

	Strength* load, psi
Loctite 414 bond	64.5/79.5
Loctite 415 bond	75.0/81.0

*Values measured on two samples; no acetone-wash, no sanding
 used to prepare surfaces.

In the actual assembling of the facemask and lens, Loctite 414 proved to be too fast in set-up time. For these reasons, a chemically identical but more diluted Loctite adhesive Loctite 420 was used.

The steps of the assembling are shown in figures appearing in Appendix A. It should be emphasized that this is a very difficult operation, requiring high speed of operation, proper equipment, and proper method of application.

The applicator we used was a Loctite Bond-A-Matic 2000 dispensing system. This consists of a closed reservoir in which an uncovered bottle of Loctite 420 was placed. Then the reservoir lid was clamped in place. The reservoir was pressurized with the help of air (approximately two-three pounds pressure). Then, the adhesive was applied from the pressurized vessel through the feed tube through the feedline to the shut-off valve in the applicator.

The Loctite 420 was applied to the lens and faceblank groove through a fine applicator needle attached to the plastic applicator head. Immediately after the use of the needle, the needle was immersed in methylene chloride to avoid solidification of the Loctite 420. The needle (as attached to the plastic applicator) was immersed into the methylene chloride until its next use. For longer idle periods, the needle-head was immersed in a jar half filled with MEK. Thus, the MEK vapor, which filled the upper part of the not fully filled jar kept the Loctite 420 liquid in the needle.

18. TOOLING AND MOLDING CYCLE PARAMETERS

As required by contract, two single cavity transfer molds were designed and fabricated - one for the faceblank, and one for the lens. Product designs were based on government furnished prototypes and castings made from tooling built to Sierra Engineering Co. Dwgs. 839-05 and 839-505 for the XM-29 mask defining product contours. These designs were modified as required to give a two piece configuration in which the lens would fit, and be adhesive bonded into, a dovetail groove in the faceblank. Mold design and fabrication was done under subcontract by Modern Mold & Tool Co. of Pittsfield, Mass., under their Job No. 7220/7618 for the Faceblank and Job No. 7221 for the lens. Contour areas for the faceblank were duplicated from government furnished castings while the lens mold was cut from castings taken from the faceblank mold to insure a fit at the dovetail groove perimeter. After completion and molding trials, the lens mold was sent out for optical finishing by Omnitech, Dudley, Mass., a division of Gentex Corp. under a separate government contract. The plunger half of the mold was plated and polished under this contract (DAAD-05-79-M-H104), but plating problems prevented finishing the cavity.

Both molds were designed as single cavity transfer molds cored for steam and water to permit temperature cycling for cure and demolding. The faceblank mold cavity was machined into split wedges with the parting line running from forehead to chin through the Outlet Valve Assembly (Ref. #3610). These cavity halves (Fig. A-1, Appendix A) were opened or closed by hydraulic cylinders and locked in place when the mold was closed by tapered wedges mounted on the top half of the mold. The core was in two sections; one fixed forming the outer perimeter of the mask including the harness straps, and the other movable and connected to the knockout plate. The face seal and chin cup on the mask were formed between the two core sections. The movable section (Fig. A-2) contained mounting locations for the mask inserts (Ref: No's. 3607, 3610, and 3605) and formed the dovetail groove at the mask/lens interface. Rubber transferred from the pot first filled a distribution pad in the center of this movable section and then flowed into the mask proper through (4) gates spaced at roughly 90° around the dovetail groove. This movable core section was the only part of the mold to be electrically heated, with control provided by a flexible lead thermocouple. The faceblank mold is shown in Fig. A-3 mounted in a Stewart Bolling 150 ton transfer press with a down acting 8" diameter transfer ram run from a separate hydraulic source.

Faceblank Mold Specifications

Dimensions:

Front to Back	18"
Height (closed)	22 1/4
Width (mold base)	23 5/8
Width (over cavity cylinders)	52 5/8
Plunger threaded	1 1/4 - 7
Estimated weight	2500 lbs

Temperature control:
(3) zones steam and water   Ref: Fig. 3 and Schematic
(1) zone electric heaters
      Watlow No's. G1E92 and G1331 (2) each 120 v. 150 w.
I/C thermocouple measurement and control

Press Requirements:

Up acting clamp stroke	76 Tons used
Down acting transfer ram	12 Tons used
Daylight	42.5" used
Pot clearance hole-top platen	6 1/4"

Knock-out plate activated by (4) 3/4" threaded rods extending
  through the lower platen to the press bed on 12" (front to back)
  by 20" spacing
Separate hydraulic source required for cavity block cylinders

The lens mold was essentially a two plate "hand mold" with a separate pot retainer plate that was unbolted at the end of each molding for pot removal and then bolted to the cavity plate to permit opening in the press. The cavity was cut into the core half with a molding material distribution pad fed by a runner from the transfer pot cut into the Outlet Valve area feeding into the lens through a curving flat gate. The lens mold is shown mounted in the same 150 ton Bolling press in the figure on P.   with the loose pot and plunger resting on the cavity plate and the retainer plate clamped to the fixed pattern.

Lens Mold Specifications

Dimensions:

Front to Back	12"
Height (closed)	9 1/2"
Width	12'
Estimated weight	350 lbs

Temperature Control:
(2) zone steam and water Ref: Fig. 6
I/C thermocouple measurement

Press Requirements:

Up acting clamp run	23 Tons used
Down acting transfer cylinder	3.25 Tons used
Daylight	31.5" used
Pot clearance hole-top platen	3.5"

Material Pressure Calculation

The pressures given in the following molding cycle descriptions are actual psi on the material. These pressures were calculated by the following formula:

$$\frac{\text{Area of Transfer Ram}}{\text{Area of Transfer Pot}} \ \times \ \text{Hydraulic psi} = \text{Material psi}$$

Note: The hydraulic psi values reported in the cycle data sheets are too high by a gage error of 120 psi.

APPENDIX A

FIGURES

Fig. 1   Faceblank mold – Cavity slide blocks ready for assembly.

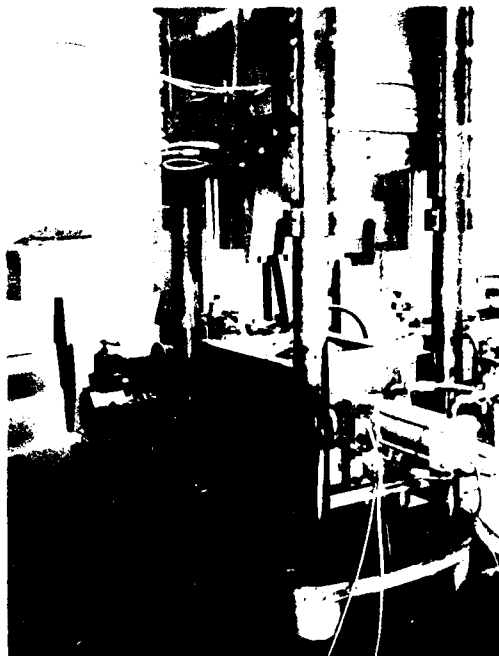Fig. 2   Faceblank mold – Core base and knockout section.

Fig. 3   Faceblank mold - Assembled in press showing hydraulic cavity block action.

Fig. 4   Faceblank mold - Demolding mask from knockout section of core.
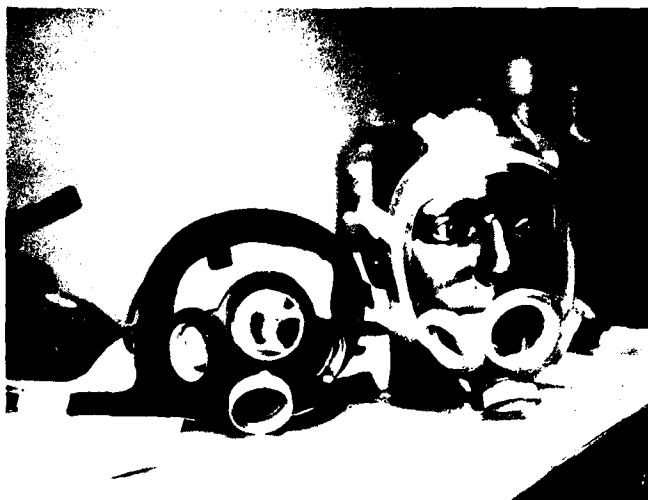
Fig. 5   Molded Faceblanks - MIL-F-51286A Rubber on left,
          Q4-2665 A&C Silicone on right.

Fig. 6   Lens Mold - Assembled in press.

Fig. 7   Lens Mold - Molded lens on core prior to demolding.

Fig. 8   Lens Mold - Demolding.

Fig. 9   Tucking lower part of lens into faceblank groove
          by spots of loctite.

Fig. 10   Tucking continued by turning platform to ensure
          loctite flows into (and not away from) groove.

Fig. 11   Filling in between and above tuck-points by in-
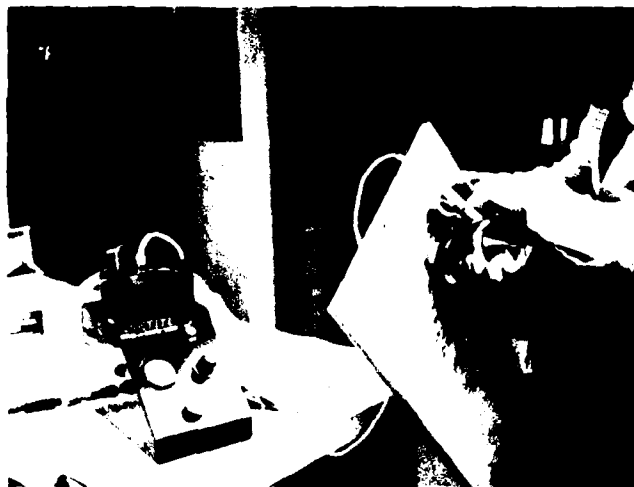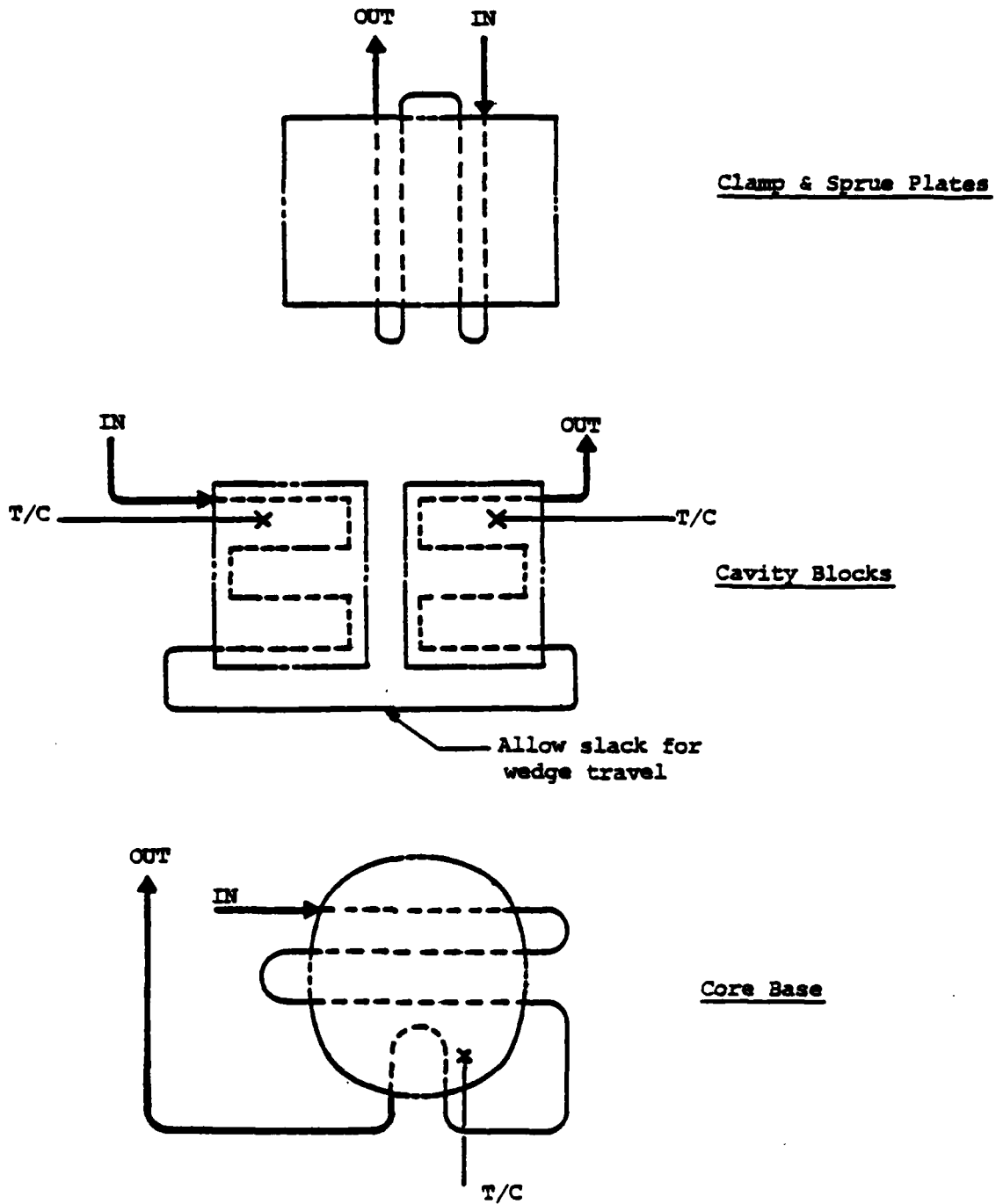jecting more adhesive through needle.

Fig. 12   Completing adhesive job by injecting loctite and
turning platform to flow adhesive into groove.

APPENDIX B

FACEBLANK MOLD PIPING SCHEMATIC

APPENDIX B

FACEBLANK MOLD PIPING SCHEMATIC

OUT   IN

Clamp & Sprue Plates

IN   OUT

T/C   T/C

Cavity Blocks

Allow slack for
wedge travel

OUT

IN

Core Base

T/C

In and Out	———
External Jumpers	———
Internal Passages	-------

Cartridge heater and T/C leads for the knockout core section
are on the right side at K-O plate level.

65
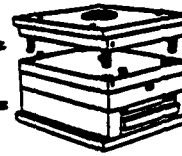
June 18, 1979

Reference: Instructions for operating cycle of
single-cavity Facemask mold.

OPEN:

1) Open parting line of mold <u>without</u> activating knock
out bar.

2) Retract hydraulic cylinder side draws.

3) Unclip straps on mask.

4) Activate knock out bar.

5) Remove inserts and strip off part.

CLOSE:

1) Load all inserts.

2) Retract knock out bar.

3) Close hydraulic cylinder side draws.

4) Close mold parting line.

APPENDIX C

FACEBLANK MOLDING CYCLE

APPENDIX C

FACEBLANK MOLDING CYCLE

Starting with a clean, cool mold mounted in the press as shown in Fig. A-3, Appendix A, cavity blocks open and core knockout section fully raised, the steps in a faceblank molding cycle were as follows:

1. Spray all molding surfaces including pot and plunger with mold release (McLube 1725 from McGee Industries, Inc. or equivalent).

2. Spray (6) head harness hole pins with mold release and load into the slots in the fixed section of the core.

3. Assemble the mold-in-place mask inserts - (2) #3607 Thread Face-piece Mounts and (1) #3605 Voicemitter Housing - onto the steel mold inserts and locate these assemblies in their seats in the core knock-out section. Check for full seating depth and tighten holding screws hand tight. The Outlet Value Assy. #3610 is fitted onto a boss seat and held in place with a screw after alignment of its external key. These components are shown in place in Fig. A-2.

4. Close the mold in stages by first raising the lower platen until the knockout core section settles into its seat in the core base. At this point, the side acting hydraulic cylinders can be activated to close the cavity slide blocks. With the cavity blocks clamped together, continue raising the lower platen until the mold is completely closed. Check for clamp pressure - 1000 psi gage used during production cycles gives a clamping force of 76 tons.

5. Preheat the mold to transfer temperature 200-220°F. This was done with 15 psi steam on the cavity block, 5 spi steam on the core base, 5 psi steam on the sprue plate, and 190°F control setting on the electrically heated core knockout section. Heat-up time was approximately 10 minutes. On the cycle record sheet and the time/temperature recording chart "0" or clock start was taken when the steam values were opened. Temperature was recorded on the cavity blocks since they had the slowest temperature response.

6. During the mold preheat time a pre-weighed charge of 350 gms of MIL-F-51286 rubber obtained from Mine Safety Appliance Co. as their compound #23050 was preheated and freshened by milling on a warm mill for about 5 minuted or until the stock temperature was approximately 170°F.

7. This charge was placed in the transfer pot and the initial "cushion" reading taken by measuring the position of the plunger in relation to the top of the pot under low transfer pressure (500 psi). Cushion readings give an inverse relation measurement of the amount of rubber in the transfer pot and were taken to confirm the initial charge and the degree of fill during the transfer period.

8. As soon as the initial cushion was taken, the transfer pressure was raised to 3500 psi and the flow of rubber into the mold monitored by cushion readings at one minute intervals. Complete fill took approximately 9 minutes, and as soon as successive cushion readings were essentially constant transfer pressure was lowered to 500 psi to reduce the amount of flash.

9. As soon as the mold was filled, steam pressure on all three zones was raised to 90 psi and 305°F control setting made on the core knockout section. A (10) minute cure cycle was initiated as soon as the recorded cavity temperature reached 300°F - a time delay of about (7) minutes.

10. At the completion of the (10) minute cure, all heat was turned off and cold water circulated through the cored zones until the recorded cavity temperature fell to the 125°F range. The time to cool was approximately (9) minutes.

11. As the first step in mold opening, the lower platen was dropped, with the transfer ram in neutral but still down, until the sprue - stretched between the sprue plate and the top of the cavity blocks - could be cut with a knife. The transfer ram was then raised to pull the cull and cut sprue out of the pot. The lower platen was then dropped until the cavity blocks were below the locking wedges - at which point they could be opened, exposing the molded faceblank. The ends of the harness straps with their cross hole pins were pulled, or pried, out of their seats in the core base to permit the knockout core section to move without stretching rubber. When all six strap ends were free, the lower platen was dropped fully, raising the core knockout section and freeing the facemask for removal.

12. The distribution pad was removed from the mask by cutting through the (4) gates. Insert assembly holding screws were removed and replaced with jack screws to pull the insert blocks from their sockets, and the outlet valve worked loose from its boss seat. The insert mount plug for the voicemitter housing was removed with the mask and separated later. The facemask was worked loose starting at the forehead edge and stretched up and forward over the knockout core. This allowed the chin cup to be worked out from under the core and pulled upward. Actual insert removal was done piece by piece during the process as its area of the mask was worked loose. A demolded facemask is shown in Fig. A-4.
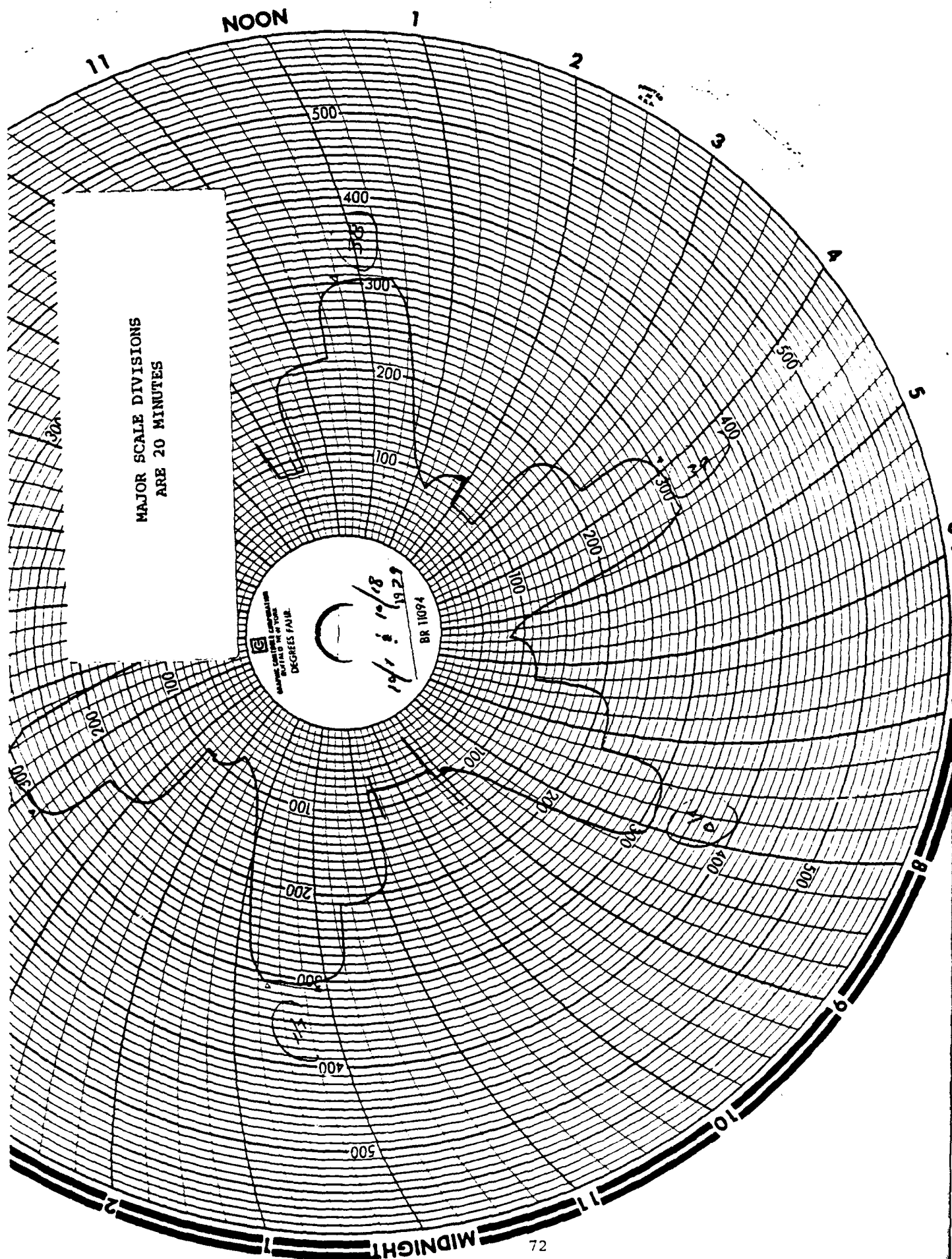
13. Removal of loose flash from core and cavity sections was the last step prior to starting a new cycle. Clock time for a cycle was in the 55 minute range ("0" set to mold open) with an overall cycle time of 80 to 90 minutes determined by demolding, clean-up, and insert loading. The actual run sheet and time/temperature chart for mask molding #39 are reproduced on the following pages along with the instructions for mold operation received from Modern Mold & Tool.

Compound # MSA
= 120 mill

Date: 10/1/39
Molding # 39

Charge wt. 340 gm.

Time	Cavity	Core	Insert/Pot		Transfer	Cushion		Clamp	Sp: Pla
0 Set	154 0	54 0	190	200	0	0		1000	54
11.2		205	195	190	200	-.06			
12					600	.70			
13						.95	.25		
14						1.16	.21		
15						1.32	.16		
16						1.42	.10		
17						1.57	.15		
18						1.19	.12		
19						1.77	.08		
20						1.85	.07		
21	90 T	90 T	305	305	200	1.86			90
30 *		302	308	288					
40 *	off								
56			128						

71

MAJOR SCALE DIVISIONS
ARE 20 MINUTES

NOON

MIDNIGHT

BR 11094

DEGREES FAHR.

72

APPENDIX D

LENS MOLDING CYCLE

APPENDIX D

LENS MOLDING CYCLE

Starting with a clean, cool mold mounted in the press (Ref: Fig. A-6, Appendix A), the steps in a lens molding cycle are as follows:

1. Check to see that bolts holding the cavity plate and pot retainer plate together are removed, and close the mold while holding the pot (from the top) seated in the clamp plate. A clamp pressure of 300 psi gage (23 tons force) was used during production cycles.

2. Load a pre-weighed charge of 80 gms molding compound into the pot and follow with the teflon seal disc, laminate pressure disc, and the loose ram in the sequence listed.

3. Lower the transfer ram to give 450 psi on the molding compound and measure cushion - distance from the top of the loose ram to the top of the transfer pot - in this case, a direct relation measurement of the amount of compound in the pot. Record the cushion reading at set "0" on the clock cycle and put the transfer ram in neutral.

4. Heat the mold (and molding compound) to approximately 225°F with 20 psi steam in both the core and cavity sections. Time/temperature recordings were taken on the cavity section since it showed a slower response than the core.

5. When the mold reached 225°F (average preheat time of 8 minutes) transfer pressure was applied, and raised to 2000 psi on the material. Cushion readings were taken at two-minute intervals to monitor cavity fill and the pressure dropped back to 450 psi as soon as constant cushion readings were obtained. Transfer was completed in the (7) minute range with mold temperature holding below 250°F.

6. As soon as the cavity filled, steam pressure was raised to 125 psi and a timed cure cycle started when cavity temperature reached 325°F. For lens moldings 44 through 56, the cure time was 20 minutes during which the cavity temperature reached 344°F. Lens moldings 57 through 81 were cured for 30 minutes at the same temperature to optimize physical properties.

7. At the end of the cure time, the steam was turned off and the mold cooled to the 135°F range with circulating water. When this temperature was reached, the press was opened, bringing the pot down with the cavity to the position shown in Fig. A-6. The pot was removed by hand for later cleaning and the press reclosed. The pot retainer plate was unclamped from the top platen, the press opened, the pot plate bolted to the cavity plate, the press closed, and the pot plate reclamped. The next press opening separated the cavity and core leaving the molded lens exposed on the core plug as shown in Fig. A-7.

8. Demolding was accomplished as shown in Fig. A-8 by slowly peeling the lens from the mold surface. No mold release was used.

The run sheet and time/temperature recording for lens molding #46 are reproduced on the following pages. Clock time for a cycle was in the 45-minute range for a 20-minute cure with a part to part overall cycle of 90 minutes.
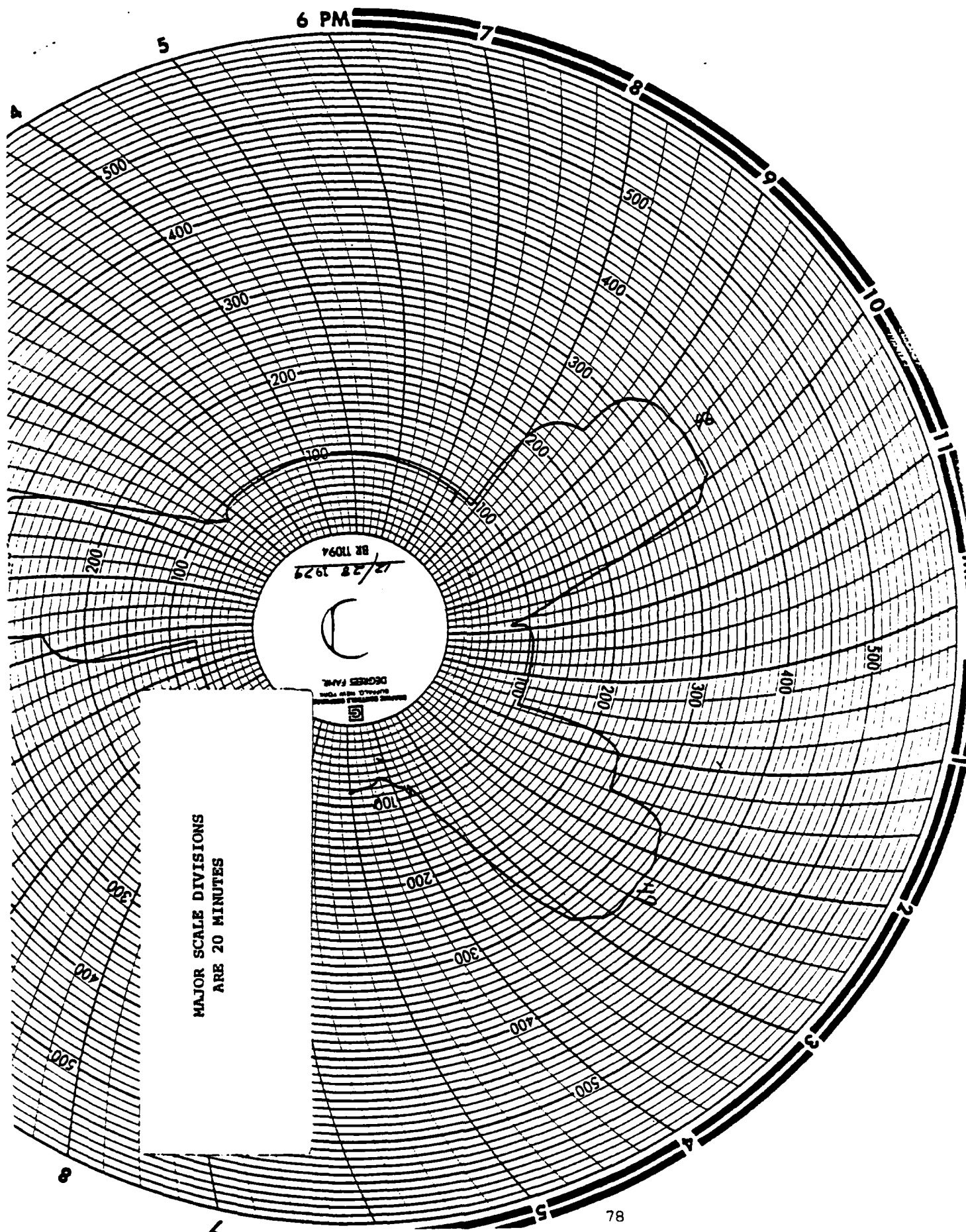
Compound # A 8247-1   Date: 12/28/79
        New ID A 10903-A
        12/14/79 Remilled 12/28   Molding # 46

                                                   Charge wt. 80gm.

Time	Cavity	Core		Transfer	Cushion	Clamp	
0 - SET	20 PSi T	20 PSi T		150/0	2 "/16	300	
8	225°			250 psi			
10	235°			"	2 3/16		
12	240°			"	1 1/2		
14	245°			"	1 3/4		
15	248°			"	1 3/8		
16 SET	120/130 T	120/130 T		150			
24	325°						
44	344°						

77

MAJOR SCALE DIVISIONS
ARE 20 MINUTES

DEGREES FAHR.

BR 11094

12/28 1979

6 PM

78

DISTRIBUTION LIST FOR ARCSL-CR-80031

Names	Copies
Commander/Director Chemical Systems Laboratory	
ATTN: DRDAR-CLJ-L	3
ATTN: DRDAR-CLJ-R	2
ATTN: DRDAR-CLW-CR	10
Aberdeen Proving Ground, MD 21010	
Commander, US Army Armament Research and Development Command	
ATTN: DRDAR-TSS	5
Dover, NJ 07801	
Administrator	
Defense Technical Information Center	
ATTN: DTIC-DDA-2	12
Cameron Station, Bldg. 5	
Alexandria, VA 22314	
US Army Material Systems Analysis Activity	
ATTN: DRXSY-MP	1
Aberdeen Proving Ground, MD 21005	